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Fenger, J.

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by

J. Fenger

Chemistry Department
Danish Atomic Energy Commission
Research Establishment Risø
Roskilde

Denne afhandling er i forbindelse med de i forordet nævnte tretten tidligere offentliggjorte arbejder af det naturvidenskabelige fakultetsråd ved Københavns Universitet antaget til offentlig at forsvares for den filosofiske doktorgrad.

København, den 11. juni 1974

Morten Lange
h. a. dec.

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PREFACE

The present report is a review of a series of studies on the chemical consequences of nuclear reactions. The investigations started in 1962 as a licentiate project in the Chemistry Department at Risø under the supervision of S. O. Nielsen; later, many experiments were carried out in collaboration with K. E. Siekierska at Risø, and some were performed during a stay with A. G. Maddock at the University of Cambridge, England. Most of the experimental results have been reported in the following papers:

1) J. Fenger, The Initial Distribution of ^{32}P-Activity in Neutron Irradiated $NH_4H_2PO_4$. Radiochim. Acta 10, 138-141 (1968).

2) J. Fenger and K. E. Siekierska, On a Correlation of Mössbauer and Chemical Data Concerning Fe^{+3} Formation by Nuclear Reactions. Radiochim. Acta 10, 172-173 (1968).

3) J. Fenger, The Initial Distribution of ^{32}P-Activity in Neutron Irradiated Salts of Phosphorus-Oxyacids. Radiochim. Acta 12, 186-192 (1969).

4) K. E. Siekierska and J. Fenger, Hot-Atom Chemistry of Iron in Iron-Oxalates. Radiochim. Acta 14, 93-99 (1970).

5) J. Fenger, K. E. Siekierska, and A. G. Maddock, Formation of Iron-57 Divalent Cation ($^{57}Fe^{2+}$) in Mössbauer Sources of Potassium Trisoxalatoferrate (III). J. Chem. Soc. A 1456-1458 (1970),

6) J. Fenger, A. G. Maddock, and K. E. Siekierska, Chemical Consequences of the Nuclear Reactions $^{58}Fe(n,\gamma)^{59}Fe$ and $^{57}Co(EC)^{57}Fe$ in Soluble Prussian Blue. J. Chem. Soc. A 3255-3261 (1970).

7) J. Fenger, Chemical Effects of the $^{31}P(n,\gamma)^{32}P$-Reaction in $K_4P_2O_7$. Radiochim. Acta 16, 42-45 (1971).

8) J. Fenger, A Mössbauer-Beam Experiment and its Possible Applications in the Study of Chemical Effects of the $^{56}Fe(n,\gamma)^{57}Fe$-Reaction. Risø Report No. 255 (1971) 18 pp. (Also as a short communication, Radiochim. Acta 17, 170 (1972)).

9) K. E. Siekierska, J. Fenger, and J. Olsen, After-Effects of the $^{57}Co(EC)^{57}Fe$-Reaction in Some Cobalt and Iron Complexes. J. Chem. Soc., Dalton Trans. 2020-2025 (1972).

10) J. Fenger and P.B. Pagsberg, Formation of ^{32}P-labelled Polyphosphates in Reactor-Irradiated Solutions of Orthophosphate. J. Inorg. Nucl. Chem. 35, 31-38 (1973).

11) J. Fenger, K.E. Siekierska, and J. Olsen, After-Effects of the Cobalt-57-Iron-57 Electron-Capture Reaction in Hexacyanocobaltate (III) Complexes, J. Chem. Soc., Dalton Trans. 563-567 (1973).

12) K.E. Siekierska, J. Fenger, and A.G. Maddock, The Fate of Recoil-^{59}Fe in an Iron Double Complex Specifically Enriched with ^{58}Fe, J. Chem. Soc., Dalton Trans. 1086-1088 (1973).

13) J. Fenger and J. Olsen, Temperature Dependent After-Effects of the Cobalt-57-Iron-57 Electron-Capture Reaction in $Cd_3[^{57}Co(CN)_6]_2 \cdot 12H_2O$. J. Chem. Soc., Dalton Trans. 319-323 (1974).

These papers and various others, dealing with experimental techniques developed in connection with the investigations, are included in the list of references pp. 98-113 with their reference numbers underlined.

The report is divided into six chapters. Chapter 1 gives a short historical introduction to the study of chemical effects of nuclear transformations; then it is shown that these effects are of significance in other fields and may even be of practical use; finally various theories and models are discussed, and it is pointed out how they may be tested. Chapter 2 reviews the available experimental techniques, with emphasis on those that are used in the investigations described below.

Chapter 3 deals with the effects of $^{31}P(n,\gamma)^{32}P$-reactions in phosphorus-oxyanions. The investigations (papers 1, 3, 7, 10) form an extension of the original licentiate project and are mainly conventional "hot-atom" studies based on radiochemical analyses of reactor-irradiated samples. Chapter 4 presents results of studies of $^{58}Fe(n,\gamma)^{59}Fe$-reactions (papers 2, 4, 6, 12); the experimental techniques are still conventional, but the approach is changed by using compounds in which the nuclear reaction can take place at different sites. Chapter 5 describes Mössbauer experiments with ^{57}Fe, which is either produced by $^{56}Fe(n,\gamma)^{57}Fe$-reactions (paper 8) or by $^{57}Co(EC)^{57}Fe$-reactions (papers 2, 5, 6, 9, 11, 13).

In the concluding chapter 6 the results and experience are shortly summarized.

1. INTRODUCTION

Virtually any nuclear reaction can have chemical consequences for the atom to which the reacting nucleus belongs. The mechanisms may differ, but in most cases the energies involved are orders of magnitude larger than those encountered in conventional chemistry; therefore nuclear transformations may initiate chemical reactions which have high energies of activation and which are therefore quite unexpected or hitherto unobserved.

High energies formally correspond to high temperatures (1 eV ~ 10^4 K), and excited or energetic atoms are for this reason said to be "hot". Hot atoms can also be produced in interactions between electro-magnetic radiation and matter or by means of accelerators.

The study of "hot atoms" - irrespective of their origin - is currently called "hot-atom chemistry"; it is closely related to studies of radiolysis and, where the processes take place in solids, to studies of radiation damage. There is, however, a difference in the approach: In studies of radiolysis or radiation damage, samples are irradiated with γ-quanta, electrons, or heavy particles; these primary quanta or particles are of little interest in themselves, but their effects are studied for various reasons and with different techniques. In "hot-atom chemistry", on the other hand, the interest is centred on the reactions of atoms that are produced in, or shot into, a sample.

Unfortunately, however, "hot atoms" are thermalized so rapidly that hot reactions cannot be followed kinetically by present-day experimental techniques, which only allow a product analysis some considerable time after the "hot" event. In all "hot-atom" studies one must therefore take subsequent reactions proceeding at lower (thermal) energies into account. These may yield information on the "hot" reactions, but are equally often studied as an object in themselves.

Under normal conditions "hot" atoms will be formed in the sample in so low concentration that they can be traced only if they are radioactive, but fortunately many nuclear reactions produce unstable isotopes that are well suited for hot-atom studies. It is, however, not possible to induce these reactions without giving the sample a dose of unwanted radiation. This can affect the reactions of the hot atoms in various ways, and for that reason few "hot-atom studies" are complete without due attention paid to possible radiolytic processes.

1.1. History of the Study of Chemical Effects of Nuclear Transformations

The development of "hot-atom chemistry" and its different aspects have been treated in a series of review articles [e.g. C3, H14, H15, M6, M28, W10, W17] and in a single monograph [S28]. The yearly number of publications on this subject has steadily increased, it was already in 1962 more than 100 [S25], and in 1970 more than 200 [A3].

Chemical effects of nuclear transformations were noticed already at the beginning of the century during the work with natural activity. Probably the first observation was made by Harriet Brooks [B24] who showed that daughter nuclei from α-decay were liberated from solid sources. Systematic studies, however, did not start until the discovery of the neutron and of artificially produced activity. In a now classical experiment from 1934 Szilard and Chalmers [S38] observed that when ethyliodide was neutron-irradiated, iodine was activated, and part of the activity was in the form of free iodine. Shortly after, Amaldi et al. [A7] explained that the iodine was liberated by the recoil from emitted capture γ-quanta. Rupture of chemical bonds can, however, also be caused by nuclear reactions with a negligible recoil. This was first shown by Segrè et al. [S13] for the isomeric transition in ^{80}Br, where the chemical effects are due to the release of an Auger cascade (cf. sect. 1.3). Chemical effects of β-decay, where there is a change in the nuclear charge and therefore in the chemical identity of the whole atom, were first studied by Mortensen and Leighton [M22].

In 1936 Glückauf and Fay [G4] discovered that atoms that were freed by a nuclear reaction were very reactive; thus by neutron activation of methyliodide, not only radioactive methyliodide and iodine were formed, but also radioactive methyleneiodide. Further it appeared that the fraction of activity that was in the parent form (the retention) decreased when the samples were diluted with an inert compound. This suggested that some of the activated atoms that were freed by the nuclear reaction returned to the parent form before the analyses. It also soon became evident that the reactions were different in gases, liquids, and solids: thus in gases the retention after neutron activation was found to be of the order of one per cent, whereas it could easily be fifty per cent in liquids or solids.

In the early studies of (n,γ)-reactions the activations were made with small neutron sources, e.g. of the radium-beryllium type [A8]. After the Second World War, however, nuclear reactors provided fluxes that were orders of magnitude larger. It then appeared [W15] that in solids the retention increased with the irradiation time, suggesting that reactions

induced during irradiation transferred activated nuclei back to the parent chemical form. Such "annealing" reactions were subsequently induced by various other treatments of irradiated samples, e.g. heating [G9], crushing [M4], UV-[C15], and γ-[C17] irradiation, or pressure [A9]; these reactions were also observed after other nuclear reactions. Recently it has been shown [A15] that the annealing reactions may depend not only on the nuclear reaction and the compound in which it takes place, but also on the amount of crystal defects in the samples, whether induced by doping, irradiation, or other treatments.

1.2. Significance of Chemical Effects of Nuclear Transformations in Various Fields

Hot-atom effects can be of practical use or present unwanted complications in many fields where nuclear reactions are applied or studied. More detailed investigations of the underlying mechanisms may therefore be justified, even where these are not of theoretical interest.

In the production and separation of radioactive isotopes [H16. S28] the fact that some nuclear reactions transfer the daughter nuclei to compounds that are different from the parent compound can be utilized. Before enriched, stable isotopes and high neutron fluxes were commonly available, the Szilard - Chalmers reaction [S38] played an important role in the preparation of radio-isotopes with high specific activity, and it is still used in special cases [A16, D9, S28, W16]. It can also be profitable to use neutron activation as a means of synthesis if a separation of the different recoil products is possible. The chemical changes, on the other hand, normally prevent a desired labelling of compounds by direct neutron activation, thus e.g. by neutron irradiation of vitamin B_{12} ($C_{63}H_{88}O_{14}PCo$) only about 1% of the ^{60}Co-activity formed is found in the parent form [M2].

A similar situation is encountered in activation analysis. The (n, γ)-recoil liberates the activated nuclei and thus makes the subsequent chemical processing and the quantitative determination independent of the parent compound. This, however, means that an analysis of molecular composition is impossible. In solids, the range of recoil nuclei is very short (cf. sect. 1.3); this has been exploited in activation analysis of sedimentary minerals to distinguish halogens bonded on the surface of grains [W2].

The radiation damage caused by (n, γ)-recoils can be important for reactor materials [e.g. C21], and has also played a role in the few cases in which transmutation doping of semiconductors has been attempted [e.g. B5].

Recoil effects associated with α- or β-decay have been an important tool in the unravelling of the families of natural radioactive elements [e.g. M15]; they are used in rapid chemical separations of shortlived fission products [e.g. H20] and in analyses of radioactive series [B23]; finally they may play a role in geochronology based on activity measurements [e.g. H9, R8].

The possibility of chemical reactions of nuclear decay can be a serious complication in some Mössbauer experiments. Normally structure analyses are made as "absorber experiments" (cf. sect. 2.4), but if the relative content of the Mössbauer nucleus in the sample is low, it is tempting to use a different procedure. Thus in principle e.g. iron containing biological material can be doped with ^{57}Co and analysed as a Mössbauer source [M26]; however, the $^{57}Co(EC)^{57}Fe$-decay may cause a change in the oxidation state of the iron - or it may even rupture the molecule to be studied. The possibility of such effects must also be considered in various other cases, e.g. when compounds of noble gases are prepared by nuclear decay and studied in a Mössbauer "source experiment" [e.g. P2, P5, P6].

Completely analogous complications may arise in studies of angular correlations of successively emitted γ-quanta [e.g. V2].

In physical and chemical experiments hot-atom events can only be studied if they occur in a large number, but in biological systems a single nuclear event can have observable effects. Thus, when ^{32}P is incorporated in a DNA molecule of viruses or bacteria, its β-decay to ^{32}S can be lethal. Similar effects are observed by incorporation of ^{33}P, the decay of which gives a very low recoil (a few eV). This indicates [A19] that the chemical effects are not caused by a mechanical recoil. Such studies may help to elucidate the biological effects of radiation [W1].

On the more speculative level it has been proposed [A5] that the reactions $^{30}Si(n,\gamma)^{31}Si(\beta^-)^{31}P$ may have played a role in the creation of life by causing formation of the important catalyst ethylmetaphosphate. It has even been suggested [A6, U2] that the optical assymmetry in some biological molecules might be related to the non-conservation of parity in β-decay!

1.3. Mechanisms and Models

Many nuclear processes have chemical consequences because they impart kinetic energy directly to the daughter nucleus via emission of particles or quanta; among these processes we will only discuss thermal neutron capture, (n, γ). In other nuclear processes the chemical effects are due to

electronic excitations or ionizations; of these we will discuss reactions that can release an Auger cascade, i. e. orbital electron capture, (EC), and internally converted isomeric transitions (IT). (n, Y)- and (IT)-reactions do not change the nuclear charge, therefore eventual chemical effects cannot simply be due to a change in chemical identity. For (EC)-reactions the effects of change in nuclear charge can be ignored if the parent and daughter elements form similar compounds (cf. chapt. 5). All these reactions further have the common characteristic that the hot atoms they produce have such a low energy that in solid samples they cannot move far from the original lattice site.

When a nucleus absorbs a thermal neutron, its binding energy (6-8 MeV) is emitted in the form of one or more Y-quanta in one of several possible cascades [e.g. H4]. A quantum with energy E_γ gives a nucleus of mass M a recoil energy of $E_\gamma^2/2Mc^2$ corresponding to a velocity of the order of 10^{14} Å/s. If it is assumed that the quanta are emitted without angular correlation and so rapidly after each other that the nucleus can be considered at rest (i. e. within 10^{-14} s), it is possible by a random walk procedure [e.g. O1] to calculate a distribution of recoil energies. Although the assumptions are never fully justified, such calculations have been attempted in a few cases [e.g. C13, C25, F3, H26, Z2]. The average recoil energy is found to be of the order of a few hundred eV, and the probability that the recoil is below e. g. 50 eV is only about 1%. Calculations with a different approach, but with similar results, have been performed by Leibfried [L2].

If the nucleus is originally sitting in an atom in a free (gaseous) molecule, the recoil energy will be divided between translation and rotation of the entire molecule and vibrations in the individual bonds. For simple molecules (e. g. CH_3I, where iodine recoils) it is possible to calculate this distribution [e. g. H27], and it appears - in agreement with experimental results [G6] - that although only the vibrational energy can be available for dissociation, at most about 1% of the molecules survive the recoil.

The velocity of the recoiling nuclei is much lower than that of their orbital electrons (~10^{16} Å/s), which therefore have ample time to adjust to the new situation. The recoil fragments should consequently be neutral or have a low charge, and for recoil reactions in gases this is confirmed by experiments [W10]. Similar results are obtained in experiments where atoms recoil out of thin (solid) foils [e. g. T4, T9].

The slowing-down of recoil atoms in an inert medium can roughly be treated like the moderation of neutrons, which is assumed to take place in

elastic collisions [e. g. L9]. The average number of collisions necessary to reduce the initial energy, E_o, of a particle of mass m_1 in collisions with particles of mass m_2, to some value, E, is:

$$\bar{n} = (\ln \frac{E_o}{E}) \Big/ (\frac{(m_1-m_2)^2}{2m_1 m_2} \ln \frac{m_1-m_2}{m_1+m_2} + 1).$$

Although it has been shown [e. g. H28] that the actual mechanisms are much more complicated, this simple formula gives good agreement with experimental observations [e. g. P8] of recoil ranges in noble gases.

Several studies have been concerned with the slowing-down and the reactions of energetic atoms in gases. Thus the Estrup - Wolfgang theory [E3, W17, M6] offers a possibility of testing whether the reactions are hot or thermal. Although the validity of this theory is debated [e. g. U4], it seems that events in the gas phase can be treated quantitatively.

In solids such calculations are hardly justified, since the recoiling atoms or molecular fragments immediately hit the surrounding molecules or ions and none of them can move freely. Therefore it is i.a. possible that some chemical bonds are broken, but that the fragments are not separated sufficiently to avoid an immediate recombination. Comparisons between nuclear reactions giving different recoil energies [e. g. Y1, Y3, Y4] suggest that 50-60 eV is necessary to give observable chemical effects. This is roughly the amount of energy which is considered necessary to produce atomic displacements in simple crystal lattices [e. g. L2]. A direct comparison, however, is dangerous, since most hot-atom studies are performed on complex, fairly open lattices.

The models which have been proposed in order to describe the effects of (n, Y)-reactions in solids have been treated in detail in many reviews [e. g. M28, S28]. In the "Ligand loss model" [L4 (1940)] based on experiments with permanganates and phosphates (cf. sect. 3. 2) Libby proposes that a central atom may "eject" one or more ligands; on subsequent dissolution of the sample (cf. sect. 2. 2) various new species, possibly with the radioactive atom in a different state of oxidation, are formed.

In the "Billiard ball model", Libby [L5 (1947)] assumes that recoil atoms are slowed down in elastic collisions. These may account for large yields of recoil atoms in the parent compound by causing replacements of the type:

$$^{80}Br + C_2H_5Br \rightarrow C_2H_5{}^{80}Br + Br.$$

Although this mechanism was originally proposed for reactions in organic liquids, it has also been invoked for inorganic solids; however, a calculation [W18 (1968)] of the expected effects for various systems shows no correlation with the experimental observations.

Willard's "Model of random fragmentation" [W13 (1953)] was likewise proposed for organic liquids, but aspects of it may have a bearing on reactions in solids (cf. chapt. 3). It is assumed that the recoil atom in the slowing-down process produces a number of radicals with which it may subsequently react - either directly or after diffusion.

Harbottle and Sutin's "Hot zone model" [H13 (1958)] is based on Seitz and Koehler's treatment of atomic displacement by irradiation [S14]. It is assumed that the recoiling atom produces atomic displacements in the slowing-down process; since a displacement requires of the order of 50 eV [e.g. L2], about six atoms are displaced for a typical recoil energy of 300 eV. In these processes the lattice is heated up, and in the model it is assumed that the entire energy is generated at one point and dissipated by heat conduction. Eventually a region comprising about 1000 atoms - corresponding to a radius of 10-15 Å - is raised to temperatures above the melting point for about 10^{-11} s. Although the disorder of a liquid may not be obtained, unusual reactions could take place in this "hot zone", and it was further argued that if the reactions were not completed before the cooling-down, reactive fragments could be frozen in and again be liberated and react if the lattice was heated. Thus there should be a possibility of obtaining information on the primary reactions by annealing experiments.

The "Hot-zone model" has been attacked by Müller [M28, M29] who has proposed the alternative "Model of little disorder" (1964-70) based on experiments with i. a. $^{185}Re(n,\gamma)^{186}Re$-reactions in crystals of K_2ReBr_6 diluted with K_2SnCl_6 [M27]. The distribution of ^{186}Re-activity over complexes of the type $ReBr_{6-n}Cl_n^{2-}$ is a measure of the probability that ^{186}Br recombines with the original ligands and thus permits an estimate of the size of the reaction zone. It was found to be of the order of 5 Å, which indicates that the damage of the lattice must be slight; this conclusion is supported by results of computer simulations of radiation damage (cf. sect. 1.4). For a further discussion cf. sect. 4.3.

Müller's results could lead to the assumption that the parent compound was reformed by an "Extreme back diffusion mechanism" [W12 (1967)],

where the recoil atom returns to the original lattice site and recombines with the original ligands. However, for a series of systems no correlation between calculated probabilities of such a process and experimental observations was obtained.

Recently Gardner et al. [G1, G2 (1970)] have investigated the effects of (n, γ)-recoil of cobalt, rhodium and iridium in ^{36}Cl-labelled $Me(NH_3)_5 Cl Cl_2$ and $Me(trien)Cl_2 Cl$. On the basis of measurements of liberated $^{36}Cl^-$, they estimate that 2-500.000 metal-chlorine bonds are broken per (n, γ)-reaction and suggest that a "Super hot zone", comprising a large distorted region of the lattice, is formed. The experimental results have been critically discussed by Rössler and Otterbach [R6]; possible the findings are due to bulk radiolysis of the samples (cf. sec. 2.1).

The above-listed models all concern the first stages in a hot-atom event, i.e. roughly the first 10^{-11} s. The subsequent annealing reactions (cf. sect. 1.1) have [e.g. H14] been discussed in terms of various mechanisms from solid-state physics. However, since these mechanisms largely ignore the role of electrons, they cannot account for various effects of crystal defects not directly connected with the reaction zone [M4]. Recently several studies by Andersen [e.g. A15] and Nath [e.g. N2] have shown how such defects can influence or possibly control the annealing reactions by release or trapping of charge carriers (cf. sect. 2.5).

A model [M5], which interprets various annealing phenomena in terms of formation of polynuclear species, is discussed in sect. 3.8.

The mechanisms responsible for the chemical effects of internally converted isomeric transitions and orbital electron capture are different from those of (n, γ)-reactions. "IT"- and "EC"-reactions result in a hole in one of the inner electron shells and can thus release an Auger cascade [e.g. B28, P9]; this may lead to the loss of several electrons - in the decay of ^{80m}Br for instance on the average 4.7 [C22]. The duration of an Auger cascade is probably 10^{-15} - 10^{-16} s [W10], i.e. shorter than the periods of vibrational motion in molecules (10^{-13} - 10^{-14} s), and consequently the atoms remain essentially fixed during the charging process. Eventually the positive charge is distributed over the entire molecule, and the potential electrostatic energy may typically amount to of the order of 50 eV. As a consequence of this, the molecule might be expected to virtually explode because of multicentre Coulomb repulsion [C6, W9], and in the gas phase this also appears to happen [e.g. C5].

In the condensed phases - especially in solids - less drastic effects can be expected. The Coulomb repulsion mechanism for chemical dissociation is analogous to that proposed by Varley [V3] and by Durup and Platzman [D11] for production of F-centres by irradiation of alkalihalides, and against these mechanisms it has been argued [e.g. D7] that a rapid electronic relaxation may prevent atomic displacement. Also, computer simulation experiments (cf. sect. 1.4) suggest that Coulomb repulsion causes little - if any - damage to simple lattices.

In some condensed systems - notably in organic halides - however, the chemical effects of Auger cascades and γ-recoil are similar. This is not in direct contradiction with the findings for alkalihalides, since the halide atoms in the organic compounds are bonded with a single bond and the surrounding lattice is fairly open.

Kazamjian and Libby [K5 (1965)] have argued that in condensed n-propyl bromide "hot" ^{80}Br-atoms formed by the $^{80}Br^{*}(IT)^{80}Br$-reaction are rapidly neutralized and are thus similar to (n,γ)-recoils.

Geislar and Willard [e.g. G3 (1963)] have presented the so-called "Auger electron reaction hypothesis" that may also apply to systems other than organic halides (cf. sect. 5.1). The electrons emitted by an Auger cascade have energies from below one hundred to several thousand eV (can be calculated from e.g. ref. H21). Unfortunately this is a region where no precise range data are available [P1], but it must be assumed that electrons with an initial energy below 500 eV dissipate a substantial fraction of it in the immediate neighbourhood of the nuclear event [C20]; electrons with energies below 100 eV may even recombine with the "mother ion" [O3]. There is thus a high probability of radiolysis of the surrounding parent molecules to form reactive fragments, and similar effects might follow the (n,γ)-recoil if the γ-decay involves converted transitions.

All the models discussed above have more or less been based on results obtained with a few related systems. Only in recent years has it been fully realized that a hot-atom event in a solid is a complex interplay of many different factors: The nuclear reaction, the parent ion or molecule, the crystal structure, possible crystal defects, and the conditions under which the processes take place. Therefore not all the observed phenomena can be described in terms of general "models" as has previously been attempted.

In hot-atom studies based on Mössbauer spectroscopy (cf. sect. 2.4) the results are normally interpreted in less general terms; some of the proposed mechanisms are discussed in chapter 5.

1.4. Computer Simulations

In recent years computer simulations have made a valuable contribution to the understanding of hot-atom events in solids. A simplified crystal lattice is postulated as an array of mass points connected by forces according to an assumed interaction potential. Then one of the atoms is given a kinetic energy or a different charge, and the subsequent processes in the lattice are followed by numerical integration of the equations of motion for all mass points.

Experiments of this type have been performed by Vineyard and co-workers on various simple lattices, i. a. copper [V6] and α-iron [E2]. It appears that the range of nuclei with energies typical for (n, γ)-recoils is normally at most a few lattice distances, and that the temperature of the lattice has fallen to below the melting point within 10^{-12} s. Some rearrangements of the atoms in the lattice may take place, but the net damage is very small.

Czjzek and Berger [C25] investigated the slowing-down of ^{57}Fe recoiling from $^{56}Fe(n,\gamma)^{57}Fe$-reactions in pure iron and alloys with Fe_3Al- and FeAl-Structure. Their method was based on calculations by Dederichs et al. [D5]; it did not give detailed information about the path of the recoiling atoms, but only calculated the number of collisions, replacements, and produced vacancies. The findings for pure iron were i. a. that 99% of the atoms leave their original lattice site and are trapped again after at most ten collisions; 82% of the atoms are trapped by replacement collisions. The findings for the alloys were similar, but a preference for replacements on iron sites was observed.

Simulations of the Varley mechanism [V3] proposed for radiation-induced atomic displacements in ionic solids (cf. sect. 1.3) have been performed by Chadderton et al. [C8]. They found that an atomic displacement of a chlorine ion in a KCl-lattice is possible only for triple or quadruple ionization of the chlorine. In a related study of the "ion explosion spike" in KCl [C7] they showed that multiple ionization of four neighbouring Cl^--ions could lead to a considerable ionic rearrangement, but that no permanent defects are formed; the whole event lasts less than 10^{-11} s. It was, however, concluded that for covalent solids, and provided the charged ions have a sufficient lifetime ($5 \cdot 10^{-13}$ - 10^{-12} s), the event may activate some of the ions to find more stable positions, i. e. the event may possibly have observable chemical effects.

All the above investigations have been concerned with very simple

systems where chemical reactions in a conventional sense are not possible. In a few cases, however, a more chemical approach has been used, and the results of one of these investigations [B27] are treated in detail in sect. 3.2.

1.5. Scope of the Investigations Reviewed

The difficulties in interpreting results obtained in studies of "hot-atom" reactions in solids are best understood by considering the time scale. In all the models (cf. sect. 1.3) it is assumed that the formation of new species and their slowing-down in the lattice are completed within 10^{-11} s; this figure is supported by computer simulations (cf. sect. 1.4). The fastest non-destructive physical techniques (cf. sect. 2.4) operate in the region 10^{-10} - 10^{-7} s; therefore the immediate chemical effects can at best only be studied by product analysis. Many annealing reactions proceed with characteristic times of minutes or more slowly and can be studied at leisure. Unfortunately, however, the most attractive technique, Mössbauer spectroscopy (cf. sect. 2.4), can only be applied in special cases, and one must therefore normally use radiochemical methods (cf. sect. 2.2) which have serious drawbacks.

The only way to obtain satisfactory information is therefore to compare results obtained with different systems and with different experimental techniques.

The investigations discussed below have mainly been concerned with reactions in phosphorus-oxyanions (chapt. 3) and in iron complexes (chapts. 4 and 5). The phosphorus system was chosen because $^{31}P(n,\gamma)^{32}P$-reactions lead to formation of a large number of labelled products and thus much information could be expected from the analyses; it was further a potential advantage that salts of phosphorous oxyacids are well suited for investigations of radiolysis by electron spin resonance spectroscopy, and that several results could be found in the literature (cf. sect. 3.1). The iron system was first of all chosen with Mössbauer experiments in mind (chapt. 5); later we found that the existence of several stable iron isotopes and some favourable properties of iron complexes permit radiochemical experiments of a new type (sects. 4.2 and 4.3).

With these systems it was planned to throw light upon the role of the composition of the matrix compound in the hot-atom event. A main point was to compare the chemical effects of nuclear reactions with radiolysis, since there is evidence from other systems that hot-atom reactions and radiolytic reactions lead to the same products. Some of the experiments

of absolute temperature. By extrapolation of the curve to T = 0, where the model requires that f = 1, it is further possible to determine f [K8]. For a further discussion cf. sect. 5.5.

A γ-quantum which has been emitted without loss of energy can, in an analogous process, be absorbed in another nucleus of the same type. However, the nuclear levels may be shifted owing to an interaction between the nuclear charge and the orbital electrons, or split owing to an interaction between a nuclear quadrupole moment and the gradient of the surrounding electrical field - a magnetic splitting is also possible, but is normally not observed in hot-atom studies. Therefore if the emitting and the absorbing nuclei are not sitting in identical lattices, it is only possible to obtain absorption if the energy of the quantum is shifted appropriately; this is in practice done by taking advantage of the Doppler effect.

In a typical Mössbauer experiment a radioactive source is moved, the emitted quanta pass an absorber, and are eventually registered with a counter. A spectrum is recorded as count rate versus velocity, and a reduction in count rate corresponds to absorption. These velocities are very small - normally of the order of mm s^{-1}. (1 mm $s^{-1} \sim 4.8 \cdot 10^{-8}$ eV).

In an absorber experiment a source which emits a single line is used - for ^{57}Fe typically ^{57}Co diffused into palladium, and the parameters of the velocity spectrum give information on the properties of the absorber. In a source experiment an absorber which absorbs only one energy is used; the spectrum then indicates the chemical form of the emitting atom. Since the γ-emitting atoms are formed in nuclear reactions, it is possible in source experiments to study the chemical effects of the nuclear reaction in question.

From the point of view of hot-atom studies, source experiments can be divided into three types, according to the reaction feeding the Mössbauer level:

1. Direct investigations of the effects of a radioactive decay, typically the $^{57}Co(EC)^{57}Fe$-decay (fig. 14). The recording of the spectra is conventional and difficulties normally only arise in connection with preparation of the sources. A series of such experiments is described in sects. 5.3-5.5.

2. "Beam" or "On-line" investigations, where the Mössbauer nuclei are generated by induced reactions in a particle beam from an accelerator or a nuclear reactor. The Mössbauer spectra are recorded concurrent with the irradiation. In studies based on accelerator irradiation it is possible to suppress the background with a pulsed beam technique [e.g. C12], but in reactor beam experiments the background can be serious problem.

An experiment with the $^{56}Fe(n,\gamma)^{57}Fe$-reaction (fig. 14) is described in sect. 5.2.

3. Investigations of induced reactions, where the Mössbauer transition does not follow immediately. Thus neutron activation of ^{118}Sn leads to formation of a 245d isomer $^{119}Sn^{*}$, which decays through a Mössbauer level. It is therefore possible to study chemical effects of the $^{118}Sn(n,\gamma)$-$^{119}Sn^{*}$-reaction by irradiation of a tin compound in a nuclear reactor followed much later by a conventional recording of its Mössbauer spectrum [e.g. A14, H12, N6]. The measurements are much simpler than in beam experiments, and it is possible to study annealing between the nuclear event and the analyses. On the other hand, it must be realized that the Mössbauer level is reached after consecutive reactions and that the actual cause of the observed chemical effects may be difficult to trace [cf. e.g. M7]. Besides tin, only tellurium [e.g. U3, W3] and osmium [R7] have been studied in this type of experiments.

In the study of chemical effects of nuclear transformations Mössbauer spectroscopy is superior to radiochemistry in that it gives a non-destructive analysis. Further, it can follow rapidly after the nuclear reaction delayed only by a time of the order of the mean life of the Mössbauer level - for ^{57}Fe about 10^{-7} s. On the other hand Mössbauer spectroscopy has two drawbacks: (1) The number of different species that can be distinguished is modest, typically two or three, where e.g. electrophoresis can easily resolve more than ten. (2) The f-factors for the different species that are not bonded identically in the lattice, may be different. In other words the species are not detected with the same efficiency, and some may not be detected at all. This crucial question is discussed in detail in sect. 5.1 and an attempt to solve it is presented in sect. 5.5.

All our Mössbauer measurements were made with spectrometers of the so-called constant acceleration type [B7, L11]. Sources were normally measured with an absorber of ^{57}Fe-enriched stainless steel and in a few cases with $K_4^{57}Fe(CN)_6 \cdot 3H_2O$. The resonances in the source spectra were identified by comparison with spectra of known absorbers; the isomer shifts for the absorber spectra were transformed [e.g. F12] to a hypothetical source experiment by a change of the sign of the velocity and a correction for the isomer shift between the absorber used in the source experiment, and the source used in the absorber experiment.

The Mössbauer spectra in source experiments are - in the nature of things - complex, and the individual resonances are broad, therefore it is

essential to resolve the spectra by computer fitting. In the present experiments this was done with a program originally developed by A. J. Stone [S29a] for the Titan computer in Cambridge, and later adapted to the IBM 360-75 at NEUCC and the Borroughs B6700 at Risø [S29b].

The resonances are fitted to Lorentzian curves by the Gauss non-linear regression procedure, and any set of parameters or linear combinations of parameters can be constrained. In most cases pairs of resonances are constrained to have equal intensity and width (quadrupole doublets), but all other parameters are left free.

2.5. Comparative Investigations
(Electron Spin Resonance Spectroscopy)

The above-described methods all detect species that contain a radioactive daughter nucleus - and those only. Important information can, however, also be obtained from studies of radiolysis and photolysis, since there may be a similarity between the inactive chemical species produced by internal nuclear reactions and by external radiation [A15, W14].

For studies of such reactions in solids a large variety of non-destructive methods are available (cf. e.g. ref. A15). Some, e.g. Mössbauer absorption spectroscopy and IR-spectroscopy, require a macroscopic decomposition of the samples, whereas others, e.g. UV-spectroscopy, measurements of electric conductivity and thermoluminescence, or electron spin resonance spectroscopy are sufficiently sensitive to detect isolated defects in an otherwise undisturbed lattice.

Most experiments only suggest what kind of species and reactions one can expect after a nuclear event, but in some cases a closer correlation is found. Thus Andersen [A11] has shown that in reactor-irradiated and subsequently heated potassium chromate, thermal annealing, emission of thermoluminescence, and changes in electrical conductivity follow the same kinetics. This indicates that the phenomena have a common cause - probably a release of charge carriers. A similar connection has been found between thermoluminescence and species formed by β-decay [A12].

In our own investigations results of electron spin resonance measurements were used in the discussion of chemical effects of $^{57}Co(EC)^{57}Fe$-reactions in cobaltihexacyanides (sect. 5.5) and of the chemical effects of $^{31}P(n,\gamma)^{32}P$-reactions in phosphorus-oxyanions (sect. 3.8). Actual measurements (sect. 3.1) were made on ammonium dihydrogen phosphate, using an X-band

Varian V-4500 spectrometer equipped with a specially constructed goniometer and a temperature regulating system [F3, F4].

Electron spin resonance spectroscopy is based on a detection of electronic spin transitions in a magnetic field. It is therefore only sensitive to species containing unpaired electrons; in solids these are: transition metal ions, certain types of crystal defects, and - of special interest in hot-atom chemistry - trapped radicals.

In a spin system consisting of an electron with spin S and a nucleus with spin I, the Zeeman energies in an outer magnetic field, H, are described by a spin Hamiltonian:

$$\mathcal{H} = \bar{S} \cdot \bar{\bar{g}} \cdot \bar{H} + \bar{S} \cdot \bar{\bar{A}} \cdot \bar{I},$$

where g and A are tensors which describe how the magnetic moment of the electron couples to the outer field and to the nuclear magnetic moment (for a popular exposition cf. e.g. ref. F6).

Some knowledge of the coupling tensors can be obtained from measurements on polycrystalline material [B20], but analyses of single crystals are far more informative. It has been shown [e.g. S12] that a determination of the maximum and minimum values of g and A with the magnetic field vector oriented in a few suitable planes in the crystal, permits a calculation of the eigenvectors of the coupling tensors. The eigenvalues of the tensors give information on the species containing the unpaired electron, and the directions of the eigenvectors indicate how these species are oriented in the crystal lattice. For an extensive review of such measurements see e.g. ref. A21.

Studies of radiolysis and photolysis are often performed on the same compounds as used in hot-atom studies, and thus direct comparisons are possible. Measurements of radiation damage, energy-range relations, channelling effects, etc. [L2] are of equal interest, but are normally performed on so simple systems that the results must be used with great caution.

were specially designed to clarify how the "retention", i.e. activity in the parent form, arises - whether it is due to a failure of bond rupture, an immediate recombination of the fragments, or subsequent annealing reactions (cf. e.g. ref. M3).

In most experiments various related solids were investigated in parallel; in the case of (n,γ)-reactions induced by reactor irradiations it was therefore essential to ensure that observed differences in the effects did not arise from different degrees of annealing or - even worse - macroscopic decomposition. This was accomplished by performing the reactor irradiations under strictly controlled conditions (sect. 2.1) and by making control experiments with labelled samples (sect. 2.3).

2. EXPERIMENTAL METHODS

When hot atoms are produced by nuclear reactions in solids their concentration in the sample is very low. Thus in a typical reactor-irradiated phosphate (cf. chapt. 3) only $1:10^{10}$ of the phosphorus nuclei have captured a neutron and formed ^{32}P. The probability that two ^{32}P are formed within a distance of e.g. 100 Å is well below 1%, and an overlap between different reaction zones (cf. sect. 1.3) can safely be ignored.

With the possible exception of reactions in semiconducters [B11, K10, O5] on the other hand, hot atoms in such low concentrations can only be traced if they are radioactive. This restricts i.a. the possible applications of electron spin resonance (cf. sects. 2.5 and 3.1) and of Mössbauer spectroscopy (cf. sects. 2.4 and 5.2).

Practically all methods in analytical chemistry have been applied in studies of chemical effects of nuclear transformations, and also many physical techniques have been tried. This chapter does not pretend to cover them all, and only the techniques that are used in the present investigations are described in any detail.

2.1. Irradiation and Annealing

Some chemical compounds have, because of their convenient properties, been used repeatedly in radiochemical studies of the effects of (n,γ)-reactions in solids, but generally the activity distributions published by different authors do not agree quantitatively (cf. sects. 3.2 and 4.1). This is undoubtedly because in general too little attention has been paid to the conditions under which samples are reactor-irradiated. Quite often facilities

intended for isotope production or activation analyses are used, and the samples receive large doses of Y-radiation and fast neutrons concurrent with the thermal neutron irradiation. Further the temperature is often not controlled. Samples irradiated in this way may still be used for annealing studies on individual compounds, but comparisons between different compounds are impossible.

Some investigations [e.g. C1, M17, S31], however, appear to be based on samples which have received so large doses (~1000 Mrads) that they must have been macroscopically decomposed. It is doubtful whether in such cases the results show anything about the chemical effects of the neutron capture (cf. sect. 4.1); this problem can to some extent be solved as described in sect. 2.3.

For the present studies a special irradiation facility was built in the thermal column at the Danish reactor DR 2. Small ampoules can be irradiated in a quartz Dewar flask embedded in one of the graphite stringers (fig. 1).

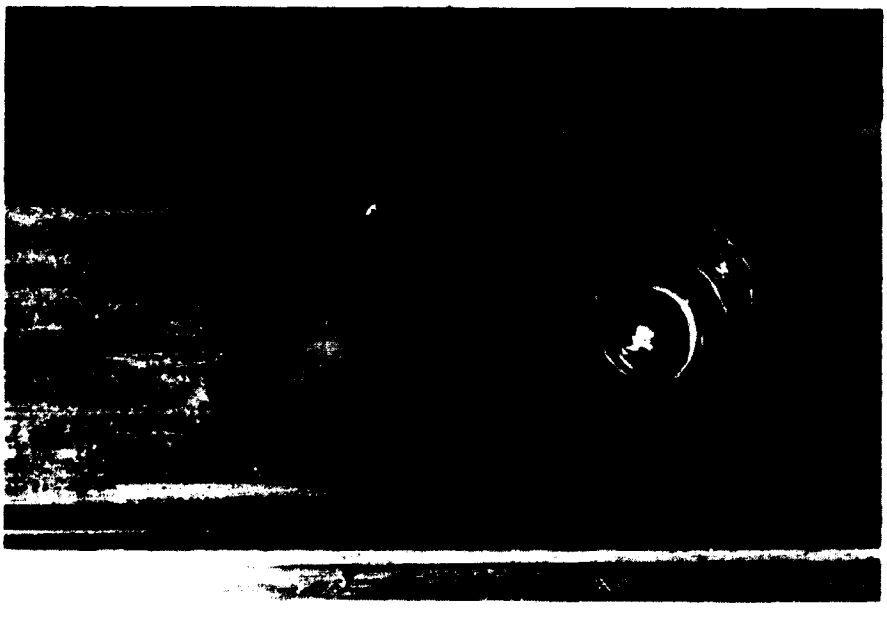


Fig. 1. Detail of the low-temperature irradiation facility at the Danish reactor DR 2. The graphite stringer lies on a rail outside the thermal column, and the quartz Dewar flask is seen standing beside the boring in which it is normally placed (nearly vertical look) [F2].

By placing the stringer at different distances from the reactor core, various sets of dose rates can be obtained. In 1963 the thermal neutron fluxes were measured with cobalt wires and the Y-dose rates with deuterated oxalic acid dosimeters [F2]. The values varied slightly with the cooling agent used, but were, in the position nearest to the core, on the average $4.5 \cdot 10^{12}$ n $cm^{-2}s^{-1}$ and 1 Mrad h^{-1} respectively; in the position farthest from the core the values were about ten times lower. Later, rearrangements of the reactor core have reduced these values by about 10% [S32]. All our comparative studies were based on irradiations with the same core configuration and thus under the same conditions.

By comparing the thermal column with other irradiation facilities at the DR 2, it can be estimated that in our irradiations the ratio between the thermal neutron flux and the Y-dose rate is up to 100 times more favourable than in most of those cited in the literature.

In studies of (n, Y)-reactions the irradiated samples are frequently annealed before the analyses; most often this is done because the resulting solid-state reactions are of interest in themselves (cf. sects. 1.1 and 1.3), but annealing may also serve as an analytical tool and give information about the nature of the labelled species (cf. e.g. sect. 3.6). Sometimes [e.g. M13] the reactor-irradiated samples are given additional doses of Y-radiation and/or thermal treatment, and the activity distributions are extrapolated back to what is assumed to be "annealing-free" reactor irradiation. Our experiments with salts of phosphorus oxyacids clearly demonstrate (cf. sect. 3.6) that this procedure is not always justified. Therefore an attempt [Y2] to extrapolate results back to before the cooling of an assumed "hot zone" (cf. sec. 1.3) must also be regarded with some scepticism.

In the present studies Y-irradiations were performed in the ^{60}Co-facility at Risø [e.g. B26] in a Dewar similar to the one used for reactor irradiations. The dose rate was of the order of 1 Mrad h^{-1}, but changed in time owing to reloading and decay of the ^{60}Co-sources.

Our samples were thermally annealed at temperatures ranging from -196°C to 300°C. In nearly all cases the same procedure, referred to as "tempering" or "stepwise" annealing was used: A number of samples were irradiated simultaneously or under identical conditions; one sample was analysed immediately and the rest stored at a fixed temperature for a certain time (normally 24 h); again one sample was analysed and the rest stored at a higher temperature and so on, until the material was thermally decomposed.

In studies by other authors a different procedure called isothermal annealing is often used; here series of samples are stored at various temperatures for varying lengths of time; this permits a determination of the activation energies in the annealing reactions [e.g. H14], but the number of analyses necessary to unravel consecutive or simultaneous reactions is much larger than in the case of tempering annealing.

2.2. Radiochemical Analysis
(Electrophoresis)

Until recently nearly all studies have followed the same pattern. After the nuclear reaction has been induced - typically by neutron activation - the samples may be annealed and are subsequently dissolved; inorganic compounds are normally dissolved in water or aqueous solutions - organic compounds in various organic solvents (ether, chloroform, etc.). The different radioactive products are separated and measured quantitatively. In the simplest cases the parent compound is precipitated, but if carriers are added for possible new radioactive products, successive precipitations or extractions may yield several fractions.

More detailed analyses can be performed by chromatographic methods [A1] which have the further advantage that they can separate carrier-free activity and thus reveal species that had not been anticipated (cf. though sect. 3.3). In analyses of samples with a low specific activity it can, on the other hand, be a serious drawback that only microquantities can be analysed (cf. sect. 4.2) unless more special techniques are employed (e.g. anion exchange chromatography or preparative electrophoresis).

If the labelled species to be separated are charged - and this is normally the case in studies of inorganic compounds - paper electrophoresis is probably the most convenient technique, i.a. because the activity scanning can be performed with high resolution [F5]. It was first used in hot-atom studies by Maddock et al. [C23]. The principle is very simple: A paper strip is wetted with an electrolyte, a suitable voltage is applied to its ends, and a small sample of the solution to be analysed is put on. The ions migrate in the electric field with a velocity which depends upon their size and charge, the properties of the electrolyte and the paper, etc. With a suitable choice of parameters it is normally possible to obtain different velocities of migration for all ions, which will thus after some time be separated on the paper. The strips are then dried and scanned for radioactivity. Peaks in the activity distribution correspond to labelled species;

they are identified by comparison with electrophorograms of known labelled ions or of ions in so large concentrations that colour reactions on the paper are possible.

In the present studies electrophoresis was used to separate ^{32}P-labelled phosphorus-oxyanions (cf. sect. 3.3) and ^{59}Fe-labelled iron complexes (cf. sect. 4.3); further it was used to check the preparation of ^{57}Co-Mössbauer sources (cf. sects. 5.4 and 5.5). Since some of the species have a limited stability, the analyses were made with a high voltage gradient (~ 35 V cm^{-1}) to ensure a rapid separation, and with efficient cooling of the strips; various aspects of such a technique are discussed in refs. M19 and W11. The experimental set-up is shown in fig. 2.

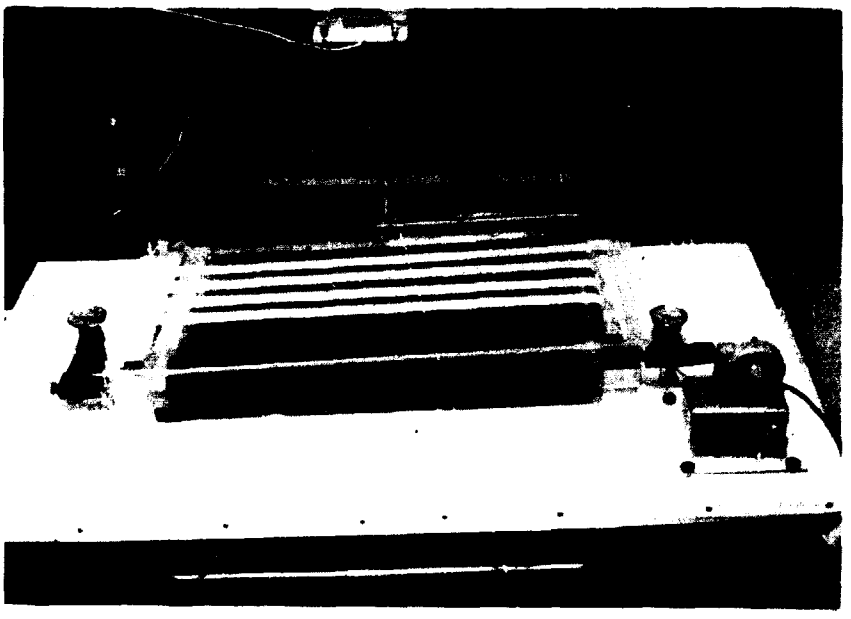


Fig. 2. The essential parts of a high voltage electrophoresis apparatus. The paper strips lie on a 90-cm long Lucite box through which a thermostated 0°C water/alcohol mixture is sucked. Together with two electrode vessels and a lid the Lucite box forms a nearly closed humid chamber.

The use of radiochemical analysis in hot-atom studies on solids is based on the assumption that there is a correlation between the labelled fragments in the solid and the species subsequently found in the solution. The justification of this assumption can be investigated by dissolving the samples at different pH [e.g. C18, C19], in different solvents [e.g. H15], or at very low temperatures [e.g. K11, V5]; also control experiments with labelled

compounds may be useful (cf. sect. 2.3). The difficulties can be exemplified by considering a neutron-irradiated crystal of NaCl. Sodium can only exist as Na^+ in water, therefore the chemical effects of the $^{23}Na(n,\gamma)^{24}Na$-reaction cannot be studied at all. On the other hand the $^{35}Cl(n,\alpha)^{32}P$-reaction yields phosphorus that is subsequently found as phosphorus-oxyanions, showing that some reaction must have taken place at dissolution [e.g. C14, S34].

2.3. Control Experiments with Labelled Compounds

In most cases we checked the thermal and radiation stabilities of the investigated compounds on material that had been labelled with the isotope to be formed by neutron activation. Samples of the labelled compounds were γ-irradiated, and subsequently annealed and analysed as if they had been neutron-activated. In the ideal case all activity should be found in the parent form, but as demonstrated by the example shown in fig. 3, it some-

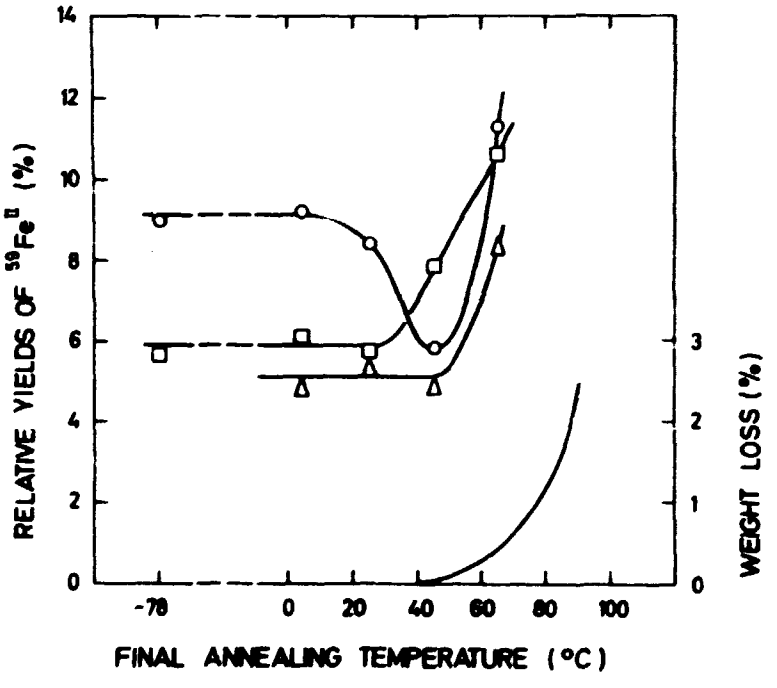


Fig. 3. A tempering annealing experiment with $Fe_2(C_2O_4)_3 \cdot xH_2O$ that demonstrates how macroscopic changes in a solid sample can interfere with the study of chemical effects of a nuclear reaction. Circles: samples reactor-irradiated at dry-ice temperature. Squares: ^{59}Fe-labelled samples irradiated at the same temperature with the same dose of ^{60}Co-γ (~5 Mrads) as received during a reactor irradiation. Triangles: labelled, unirradiated samples. The curve to the right shows the weight loss as measured by thermogravimetry [S20].

times is not. In these experiments ferric oxalate was labelled with ^{59}Fe, and after different treatments analysed for $^{59}Fe^{II}$ (cf. sect. 4.1). The results show that for three reasons a thermal annealing curve for reactor-irradiated ferric oxalate cannot be interpreted directly. (1) Even in untreated labelled material about 5% of the activity is found as $^{59}Fe^{III}$; this suggests that either the samples are not pure, or the analysis introduces an electron exchange between Fe^{II} and Fe^{III} [S19]. (2) When the material is heated to about 50°C, a thermal decomposition starts, and it results in a sharp increase in the yield of $^{59}Fe^{II}$. (3) For material which was in addition γ-irradiated before the analysis, the $^{59}Fe^{II}$ yield was even higher, although the same pattern was observed.

For the special compounds containing iron atoms in two different chemical forms similar experiments with specifically labelled samples were used to establish that no disturbing isotope exchange took place during the irradiation, annealing, and analyses (cf. sects. 4.2 and 4.3).

We find it surprising that control experiments of this type are very seldom reported in hot-atom studies; they would in all probability have revealed a macroscopic decomposition of the reactor-irradiated samples in many studies (cf. sect. 2.1).

2.4. Non-destructive Physical Methods (Mössbauer Spectroscopy)

Obviously any analysis based on solution chemistry only presents a phantom of the situation in the solid since only species that exist in the solvent can be observed; there has therefore been a growing interest in the use of non-destructive physical methods in hot-atom chemistry. The time scale of the events (cf. chapt. 1) shows that it will be difficult - if not impossible - to follow the direct effects of a nuclear reaction kinetically. Some information on the slowing-down of recoil atoms may be obtained from measurements of nuclear resonance fluorescence [e.g. A4], but so far all investigations have been concerned with decay of nuclei that have come to rest in the lattice.

The decay of a radioactive atom is influenced by its chemical state in various ways [H22, P4, V2]. Thus in different compounds the half life may vary by the order of 1% [A22, M9] and the energy of emitted Auger electrons by a few eV [e.g. F1, H1 and various papers in ref. F20]. This offers - at least in principle - possibilities of chemical identification.

However, only two effects have been of practical use: the chemical influence on the energy of emitted γ-quanta, as measured via the Mössbauer effect [e.g. F22], and the perturbation of the angular correlation of successive quanta [e.g. K3]. Results of measurements of perturbed angular correlations are difficult to interpret [e.g. B2, V1] and normally [e.g. S7] only suggest that the decaying nuclei can occupy other lattice sites than suggested by radiochemical analysis; in some cases no effects are observed [V4]. Mössbauer spectroscopy, on the other hand, is now a well-established tool in hot-atom chemistry [A2, M7, W7, W8].

Mössbauer spectroscopy [e.g. F22] is based on recoilless emission and absorption of nuclear γ-quanta - the so-called Mössbauer effect, which has so far been observed in about 75 nuclear transitions [B10]. If an atom is incorporated in a crystal lattice, its nucleus can emit or absorb a γ-quantum without loss of energy, provided that no lattice vibrations are excited. The probability of such processes - the so-called f-factor - depends upon the γ-energy and the mass of the nucleus, and upon the properties of the lattice and its temperature. To a first approximation [e.g. K8] the f-factor can be expressed by the relation:

$$f = \exp\left(-\frac{E_\gamma^2}{mc^2}\,\frac{1}{\langle(\hbar\omega)^2\rangle}\,kT\right),$$

where $\langle(\hbar\omega)^2\rangle$ is the mean square of the frequency spectrum of lattice vibrations, which can only be calculated in very simple cases. Introducing the Debye temperature, θ_D, by the relations

$$\hbar\omega_D = k\theta_D \qquad \text{and} \qquad \hbar\bar{\omega} = 3/4\ \hbar\omega_D,$$

it is possible to obtain the following "high temperature approximation" [e.g. G8] valid for temperatures above about $1/2\theta_D$, i.e. for most inorganic salts above liquid-nitrogen temperature:

$$f = \exp\left[\frac{-6E_\gamma T}{k\theta_D^2}\right],$$

where E_γ is the γ-recoil energy ($1.95 \cdot 10^{-3}$ eV in the case of ^{57}Fe) and k is the Boltzman constant ($0.862 \cdot 10^{-4}$ eV deg.$^{-1}$). This allows a determination of θ_D from semilogarithmic plots of resonance intensity as a function

3. REACTIONS IN SOLUTIONS AND SALTS CONTAINING PHOSPHORUS-OXYANIONS

The well-known tracer isotope ^{32}P has been very popular in hot-atom chemistry [H7], both when produced by various nuclear reactions and when accelerated as ions. The reaction $^{31}P(n,\gamma)^{32}P$ (fig. 4) is well suited for the study of chemical effects of thermal neutron capture. ^{31}P has 100% natural abundance and a reasonable activation cross section (0.23 b). The decay of the excited ^{32}P is fairly well known [N5], and it is possible to estimate the γ-recoil distribution, which has a maximum energy of 1057 eV [C13, F3]. All transitions are of low multipole order, and therefore internal conversion is insignificant [L10]; any chemical effects which may be observed can thus be due to γ-recoil only. Ground-state ^{32}P has a convenient half life (14.3 d), and since it decays by emission of high-energy β^- only, it is easy both to detect and shield.

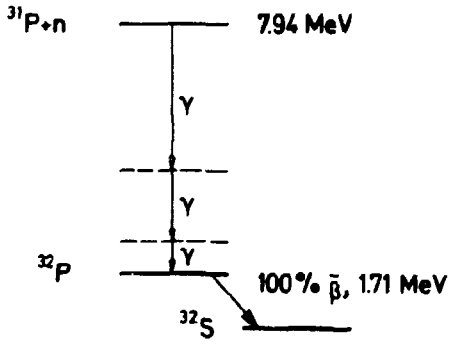
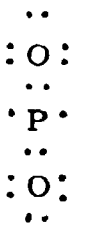
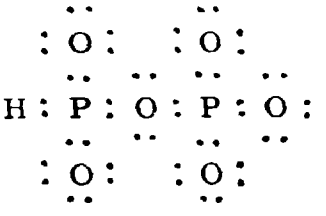


Fig. 4. The $^{31}P(n,\gamma)^{32}P$-reaction.

Phosphorus forms a series of oxyanions from monomers, like orthophosphate, to polymers of almost unlimited complexity [W4]. A "polymer" is here and below taken to mean a species with more than one phosphorus atom. The lower phosphorus oxyacids have been extensively studied by i. a. Blaser and Worms whose structural notation [B17] is commonly used. In all stable phosphorus-oxyanions observed so far the phosphorus is present in the configuration:



In the stable forms of the monomer anions (hypophosphite, phosphite, phosphate) the two free valencies are saturated with H· or :Ö· ; in polymers the PO_2^--group is connected with one or two similar groups, either directly or through ·Ö· . Therefore the P-O skeleton and the states of oxidation of the P-atoms can describe the structure of an ion; thus e.g. the isohypophosphate anion



is simply denoted P^3-O-P^5. In these oxyanions phosphorus in states 1, 2, and 3 is bonded to hydrogen, and phosphorus in states 4 and 5 is not. Below these states are referred to as "reduced" and "oxidized" respectively. However, since phosphorus is covalently bonded in almost all its compounds [W4], the state of oxidation is merely a formal concept.

The phosphorus oxyanions can be conveniently separated by chromatographic methods, and most of them are so stable in aqueous solution that they do not react measurably at temperatures near $0^{\circ}C$. Exchange of phosphorus isotopes between different anions has been observed after prolonged heating [B19], but under normal conditions it can safely be ignored [H30, W4].

The alkali-metal and ammonium salts of these acids form a system which is well suited for the study of the chemical effects of the $^{31}P(n,\gamma)^{32}P$-reaction in solids. Our own investigations [F3, F7, F10, F13] have covered twenty-eight salts with different anions and cations, and different content of crystal water. In addition, aqueous solutions containing phosphate ions were studied [F17]. The analyses were in all cases performed by high voltage paper electrophoresis (cf. sect. 3.3).

The radiation chemistry of phosphorus compounds has been reviewed by Halmann[H8] in 1967. Reactions in solutions have recently been reviewed in papers by Grabner et al. [e.g. G7].

In solution, phosphite can be oxidized to phosphate by radiolytically produced hydroxyl radicals, but irradiation of aqueous orthophosphate did not produce significant amounts of reduced phosphorus oxyacids. Large doses applied to solutions of hypophosphite and phosphite result in formation of dimers, possibly via formation of phosphite radicals. These phenomena are discussed in sect. 3.4.

Radiolytic reactions in solid salts of phosphorus oxyacids have been extensively studied by ESR-spectroscopy (cf. sect. 2.5). The results are reviewed in sect. 3.1.

Below our ESR-measurements (sect. 3.1) and our experiments with solutions (sect. 3.4) are described first since they offer a clue to the understanding of the chemical effects of $^{31}P(n,\gamma)^{32}P$-reactions in solids (sects. 3.5-3.7). Actually the experiments were performed in a different order, and it appears that some of the hyphoteses put forward in refs. F7, F10, and F13 are not tenable any longer.

3.1. Radiolytic Products in Solid Salts of Phosphorus-Oxyanions. ESR-Measurements

Several phosphorus-containing radicals have been identified by electron spin resonance spectroscopy of irradiated salts of phosphorus oxyacids [e.g. A21]; most salts were irradiated with γ-quanta with energies about 1 MeV, but X-rays appear to have the same effect [H5].

In orthophosphates [S33] the most important stable radical is PO_4^{2-} with a hyperfine structure coupling (the A-tensor, cf. sect. 2.5) of about 29 gauss. In some orthophosphates a slightly higher hyperfine structure coupling is observed; this may be explained by a protonation of one of the oxygen atoms to form $HOPO_3^-$. In pyrophosphates the radical $P_2O_7^{3-}$ and possibly $HP_2O_7^{2-}$ is observed [S33]. In polyphosphates [H18, H29, K2] the predominant radical formation seems to be trapping of electrons or holes on PO_4-chain groups; there is, however, also some indication of P-O-P bond rupture to form $-PO_3$ and $-PO_4$ end groups with unpaired electrons.

In the phosphites $MgHPO_3 \cdot 6H_2O$ [H11] and $K_2HPO_3 \cdot 5H_2O$ [H24] irradiation results in rupture of the P-H bond to give the PO_3^{2-}-radical. Also in $NH_4H_2PO_2$ [M23] a P-H bond can be ruptured, resulting in formation of the HPO_2^--radical. This radical can - within a few days at room temperature - react with an adjacent $H_2PO_2^-$-ion, forming the $O_2P\text{-}PHO_2^{2-}$-

radical. The reaction requires translation of the two species of 1-2 ångström; this is possible since the lattice is fairly open [Z1] and the ions in the lattice are not strongly fixed by hydrogen bonds as e.g. in KH_2PO_4.

Y-irradiation of $(NH_4)_2H_2P_2O_6$ [M24] results in the trapping of the radical $O_2P\text{-}PO_3^{3-}$. On heating of the crystals to about 120°C the P-P bond breaks, the products being PO_3^{2-} and (presumably) PO_2.

From the above it must be concluded that ionizing radiation can cause the rupture of a P-H bond which seems to be a weak point of attack (cf. also ref. L8); rupture of P-O bonds is more rare and displacement of central P atoms is unlikely. The directions of the eigenvectors (cf. sec. 2.5) of the hyperfine structure tensors indicate that the radical fragments normally remain, correctly oriented, in the lattice site. Only in Li_3PO_4 was a rotating PO_4^{2-}-radical observed [S33]. Observations made with similar central atom systems are completely analogous [e.g. A21] (cf. also sect. 5.5).

In our studies ESR-measurements were made on single crystals of ammonium di-hydrogen phosphates that were irradiated and stepwise annealed in the same way as in the tempering experiments mentioned in sect. 3.6. Three sets of crystals were reactor-irradiated under the same conditions as used for studies of $^{31}P(n,\gamma)^{32}P$-reactions (cf. sect. 3.6). (1) $NH_4H_2PO_4$, with normal isotopic composition, (2) $ND_4D_2PO_4$, deuterated to 98%, and (3) $^{15}ND_4D_2PO_4$, deuterated and further enriched in ^{15}N to 96%.

The observed ESR-lines fall in two groups, one contains a system of resonance lines in an interval of 100 gauss around g = 2, and one consists of a number of doublets with spacings of 500 gauss. The centre part of the spectra was of the same intensity for the three crystals, although the pattern was simpler for the deuterated forms. The outer part of the spectra had the same intensity for the $NH_4H_2PO_4$- and $ND_4D_2PO_4$-crystals, but was reduced to about 1/10 in the $^{15}ND_4D_2PO_4$-crystals. If $NH_4H_2PO_4$ was given pure Y-doses similar to the ones received during reactor irradiation, the centre part was the same, but the intensity of the outer part corresponded to that of reactor-irradiated $^{15}ND_4D_2PO_4$.

From the above it is concluded that the centre part of the spectra arises from Y-induced species. They were not conclusively identified, since the lines were strongly overlapping, but the low hyperfine structure coupling suggests structures like PO_4^{2-} and $HOPO_3^-$.

The outer spectrum is attributed to a species predominantly formed as a consequence of the $^{14}N(n,p)^{14}C$-reaction which is prevented by substituting

^{15}N for ^{14}N. A determination of the g- and A-tensors (cf. sect. 2.5 and fig. 5) shows that the lines must arise from radicals in eight equivalent lattice sites with coupling tensors axially symmetric around P-O bond directions. The principal values of the A-tensor are similar to those previously found for the PO_3^{2-}-radical [H11, H24], and it was therefore concluded [F3] that oriented PO_3^{2-}-radicals had been produced by the displacement of oxygen atoms. The number of PO_3^{2-}-radicals in the crystals was found to be in reasonable agreement with the estimated number of atomic displacements produced by recoiling protons and ^{14}C-atoms from the $^{14}N(n, p)^{14}C$-reaction.

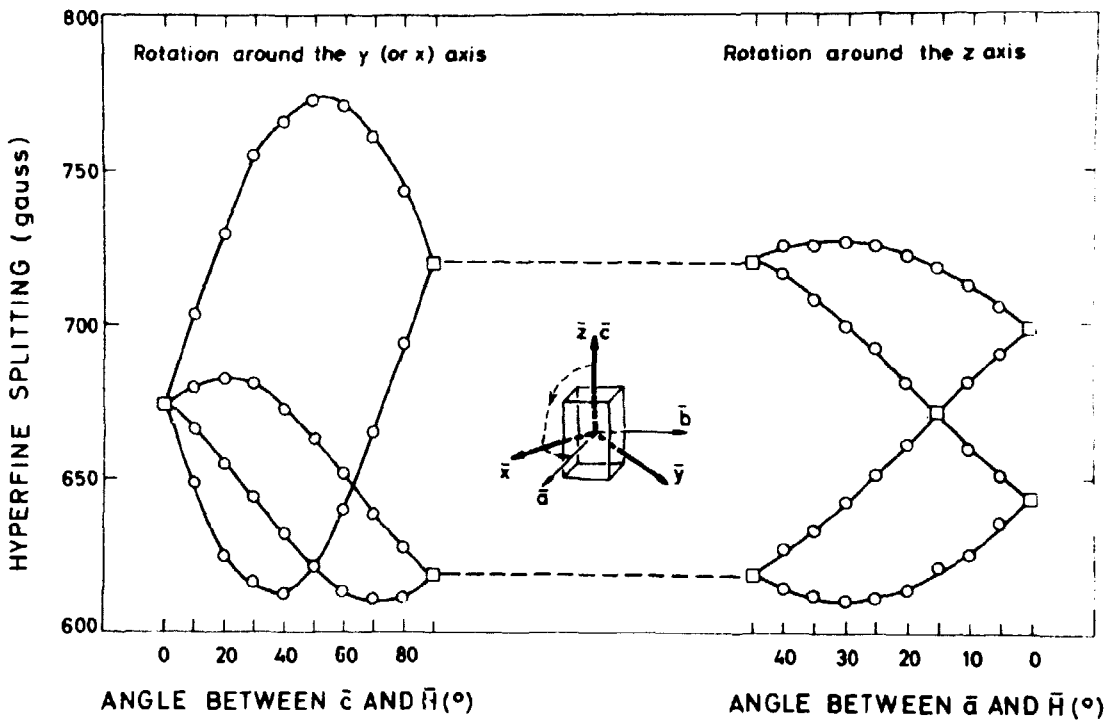


Fig. 5. Determination of the A-tensor for the PO_3^{2-}-radical in a single crystal of $ND_4D_2PO_4$. The crystal was reactor-irradiated at 4°C for 24 min. ($4.5 \cdot 10^{12}$ n cm^{-2} s^{-1}, 0.8 Mrads/h) and measured at -20°C with various orientations in the magnetic field (ν = 9.132 10^9 c/s). From the extremum values the "eigenvalues" are calculated to be: $A_{\parallel}$ = 2167 Mc/s; $A_{\perp}$ = 1691 Mc/s.

Our results are in agreement with the previous observations that γ-irradiation has a low probability of P-O bond rupture in phosphates, but we have shown (to our knowledge for the first time) that this bond rupture is readily produced by energetic heavy particles. Similar results were later obtained in investigations [P7] of the influence of radiation on the ferroelectric phase transition and dielectric properties of KH_2PO_4; measurements of these effects do not give detailed information on the radiation damage, but they are, on the other hand, not restricted to the detection of radicals.

It was impossible to find any correlation between thermal annealing of ^{32}P-labelled species (cf. sect. 3.6) and annealing of trapped radicals; therefore it seems improbable that ^{32}P-labelled fragments themselves should be of the PO_3^{2-}-form. On the other hand hot recoil-^{32}P might produce non-radioactive phosphite radicals and react with them; this possibility is discussed i. a. in sect. 3.5.

3.2. Previous Investigations of $^{31}P(n,\gamma)^{32}P$-Reactions in Phosphates

The first experiments with neutron irradiation of inorganic phosphates were performed in 1940 by Libby [L4]. He only distinguished two fractions of ^{32}P, one which was precipitated as magnesium ammonium orthophosphate, and one which was not. The precipitate was shown to contain about 50% of the total ^{32}P-activity, almost independent of the irradiated compound and of whether it was solid or in solution. It was therefore concluded that about half the recoil processes result in the ejection of oxygen - thus lowering the "state of oxidation" of ^{32}P - whereas the other half leave ^{32}P as orthophosphate or in a state that is readily oxidized. However, it later (~1952) became evident that this model was too simple, since various observations [A20, F21, M1] indicated the formation of condensed phosphorus-oxyanions labelled with ^{32}P.

Soon after the introduction of paper electrophoresis in the separation of phosphorus-oxyanions [S8] Lindner and Harbottle [L7] found more than ten different ^{32}P-labelled anions, nine of which they identified. Later other chromatographic methods have been shown to give equally complex activity distributions, but in spite of the similarity in the analytical techniques employed by different authors, the intial distributions of ^{32}P over different phosphorus-oxyanions for given salts have not been agreed upon. In most cases it is possible to explain the discrepancies by differences in

the conditions under which the samples were neutron-activated. Generally, higher temperature results in larger yields of ^{32}P in high oxidation states (compare e.g. the results in refs. A10, C16, L7), irradiation at temperatures above $0^{\circ}C$ may further result in lower yields of polymer species, and in the extreme case [S9] activity is found in the parent form only. Also the concurrent Y-irradiation is of importance since some phosphates are very sensitive to radiation annealing [C15, T1] (cf. sect. 3.6).

Some discrepancies, however, are not so easily dismissed. Lindner [L7] found little evidence of species more complex than tripolyphosphate, and later he showed [L8] that in orthophosphates the tripolyphosphate was mainly centre-labelled, suggesting that a ^{32}P-labelled fragment was caught between two PO_4^{-3}-ions in a nearly undamaged lattice. In pyrophosphate the tripolyphosphate was endlabelled, suggesting that the ^{32}P was linked to one end of the $P_2O_7^{4-}$-ion. In these later experiments the tripolyphosphate was precipitated as the tris(ethylenediamine)-cobalt(III)salt, which was subsequently hydrolyzed into pyrophosphate and orthophosphate to show the ^{32}P-position. It is worth noting that with this procedure the total yield of tripolyphosphate was considerably higher than in the earlier analyses with electrophoresis (for e.g. $Na_2HPO_4 \cdot 2H_2O$ 13% [L8] against 5% [L7]). Possibly some of the previously unidentified ^{32}P-labelled species coprecipitate with the tripolyphosphate.

In striking contrast to Lindner's studies, Anselmo [A17, A18] analysed neutron-irradiated phosphates, phosphites, and hypophosphites with ion exchange chromatography and claimed that a considerable amount of ^{32}P-activity was present in the form of species containing more than fourteen phosphorus atoms; he suggested that the recoils produce much fragmentation in the crystal lattice, and that the fragments combine to polyphosphates when the samples are dissolved for analysis.

Ujimoto et al. [U1] investigated the separation of phosphorus-oxyanions by anion exchange and gel chromatography; they found that the separations of ^{32}P-labelled anions with and without carrier differ considerably, and suggested that some carrier-free ^{32}P-labelled species can be adsorbed on the chromatographic column. Since this activity is more difficult to elute, it can erroneously be attributed to higher polymers.

Taking these carrier effects into account Nakamura et al. [N1] have analysed several irradiated phosphates by ion exchange chromatography; they found a few per cent of ^{32}P in species containing six or more phosphorus atoms, and suggested that ^{32}P-labelled polyphosphates are formed by thermal condensation in a hot zone.

Several studies of salts of phosphorus oxyacids have been centred on annealing of ^{32}P back to the parent form by thermal treatment [B1, C16], γ-irradiation [T1], UV-exposure [C16], or compression [A10]. Some of the results are discussed in the following sections.

A trajectory study (cf. sec. 1.4) of ^{32}P-recoils in sodium phosphate [B27] is one of the very few computer simulations in hot-atom chemistry. In the models, phosphate ions, with none, one, or two oxygens protonated were fixed in a fictitious cubic unit cell; in some cases the phosphate ions were surrounded with particles of mass 18 to simulate crystal water. Since the charges of the recoil fragments were not known, simplified interactions between the atoms were assumed. The starting conditions were chosen to correspond to a randomly oriented velocity of the central phosphorus atom, characteristic recoil energies being estimated from the γ-decay of excited ^{32}P. The results indicate that the recoiling ^{32}P at first behaves as if it was a free particle that moves until it hits something. In this first encounter the chemical nature of the object struck is relatively unimportant, and the probability that the ^{32}P-recoil will escape its original lattice cell depends mostly upon the number of atoms in the cell. In an anhydrous crystal it is likely to get away, but with water molecules present this may be considerably more difficult. Possibly oxygen atoms are emitted from the recoil site, but the P-O bond is hardly ever preserved. It was suggested that ^{32}P in reduced monomeric forms (P^1, P^3) arises from ^{32}P- and O-ejection followed by reflection of ^{32}P back to the original site. Dimeric species are assumed to represent migration of P to the next lattice site, whereas formation of higher polymers requires traversal of more than one neighbouring P-site. Since most of the penetration power of the recoil-^{32}P appears to be used in the escape from its original cage, the yield of species containing more than two phosphorus atoms should be low.

These mechanisms are different from the ones assumed by Libby in the "Ligand loss hypothesis" (cf. sect. 1.3 and ref. L4) although the net results may be similar. The computer results on the whole explain Lindner's findings [L7], but the findings of Nakamura [N1] cannot be completely dismissed, since it was not established to what extent a lattice could be damaged by emitted oxygen atoms. Our own studies of these problems are treated in sects. 3.5-3.7.

$^{31}P(n,\gamma)^{32}P$-reactions in solutions have recieved little attention since Libby's work in 1940. Recently, however, two groups [K14, K15, M13] have demonstrated the formation of ^{32}P-labelled polymers in solutions con-

taining various phosphorus oxyacids. The polymers were largely identified as P^2-P^4 and P^4-P^4, but may equally well have a P-O-P structure, since complete separations were not obtained. Similar products have been found in γ-irradiated aqueous solutions of hypophosphite [K16] and phosphite [M14], and it is suggested [K14] that the polymerization in neutron-activated solutions is caused by radicals formed in concurrent γ-radiolysis. This interpretation is not in agreement with the results of our studies of $^{31}P(n,\gamma)^{32}P$-reactions in solutions (cf. sect. 3.4).

3.3. Separation of Phosphorus-Oxyanions by Electrophoresis

In view of the large number of ^{32}P-labelled species that may be formed in neutron-activated salts of phosphorus oxyacids, it is natural to use a chromatographic method for analysis [K12]. For the present studies, high voltage electrophoresis was chosen (cf. sec. 2.2). The activity peaks, corresponding to ^{32}P-labelled species, are identified by running macroscopic amounts of known ions that are then found on the paper by the molybdenum-blue reaction [H10].

In a series of preliminary experiments the separations were made as described by Lindner [L7], using a supporting electrolyte of 0.1 M lactic acid on untreated Whatman 3MM paper. This, however, did not give satisfactory results. Commercial orthophosphates apparently contain a slight amount of pyrophosphate; therefore $^{32}P^5$-O-P^5-anions are not carrier-free and can be precipitated with metal ion impurities in the paper. Consequently the $^{32}P^5$-O-P^5 was found near the starting point, smeared out in an irreproducible way; this effect may account for some uindentified activity reported by other authors [A10, C16, L7]. A careful washing of the paper in 1 N HCl and redistilled water prevented the precipitation of pyrophosphate, but its velocity of migration was now inconveniently close to that of other anions.

In the final version of the analysis the $^{32}P^5$-O-P^5 was deliberately precipitated at the starting point by dissolving the samples in a solution containing 0.1 M lactic acid and 0.1 M pyrophosphate and using an electrolyte of 0.1 M lactic acid and 0.05 M zinc acetate (pH = 4.3) [S8]. Up to fourteen different fractions are distinguished; one of the most complicated activity distributions is shown in fig. 6. The simple distribution below demonstrates the width of simple, well-separated peaks.

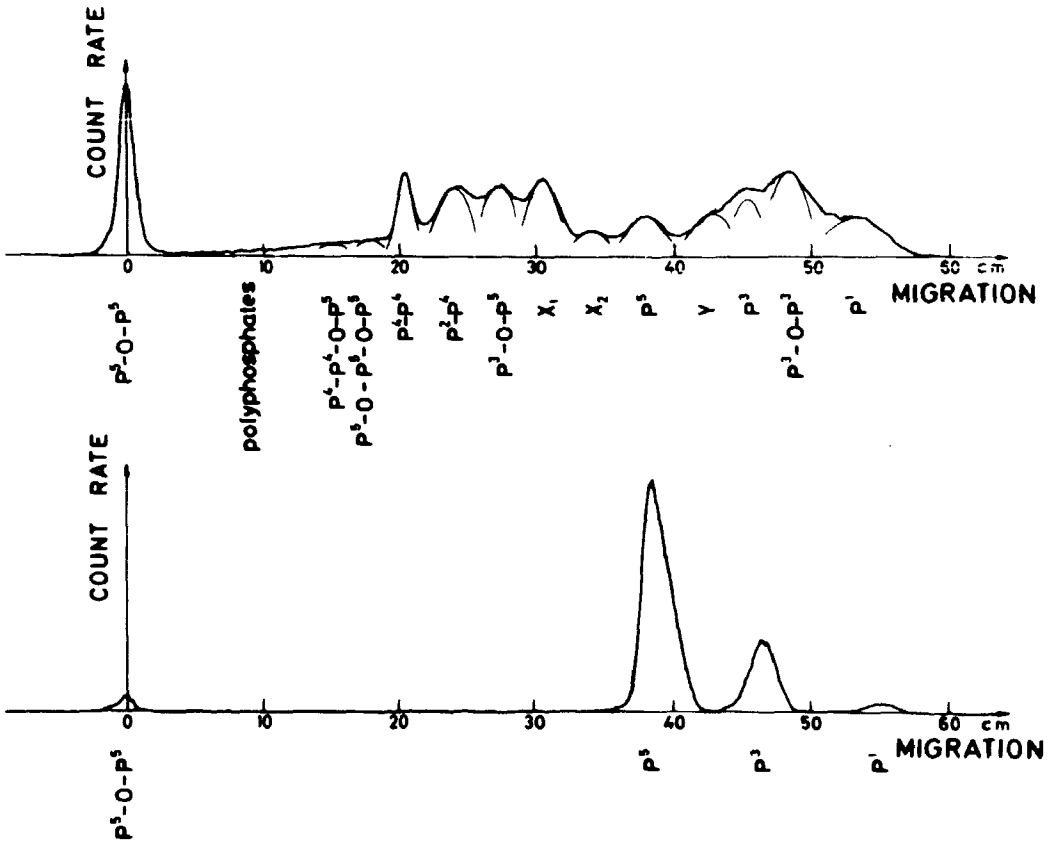


Fig. 6. Electrophoretic separations of ^{32}P-labelled phosphorus-oxyanions. The upper one, obtained with a solution of reactor-irradiated $Na_2H_2P_2O_5$ (P^3-O-P^3-anion), demonstrates the relative positions on the paper of the individual anions after separation; the lower one, obtained with a reactor-irradiated solution containing orthophosphate, demonstrates the width of the individual activity peaks [F10, F17].

Four fractions, in fig. 6 denoted "polyphosphates", X_1, X_2, and Y, have not been conclusively identified. The Y-anion is assumed to be P^2-P^2 [B12] since it has a high velocity of migration and all other known anions with one or two P-atoms are found elsewhere on the paper. The polyphosphate fraction probably contains various anions with more than three P-atoms, but the yields were in all cases so low that a resolution into individual peaks was not possible.

More important is the nature of the anions X_1 and X_2. They were first seen in experiments with $NH_4H_2PO_4$, which was neutron-activated at liquid-nitrogen temperature and immediatedly dissolved [F7]; later high yields were obtained from hypophosphites and various salts with complex anions - notably those containing phosphorus in a reduced state [F10]. Probably

the X-anions are related to the P^3-O-P^5-anion to which the labelling ^{32}P-activity is transferred, when the irradiated crystals are stored at dry-ice temperature before the dissolution, or when the solutions are stored for a few days before the electrophoretic separation [F7, F10]. P^4-P^4-O-P^4-P^4, P^4-P^3-P^4, and P^3-O-P^4-P^4 can be excluded on the basis of their velocity of migration [D6, F13]. $(-P^3-)_6$ and $(-P^4-P^4-O-)_2$ have largely the correct positions on the paper [D6], but can hardly undergo the observed transformation.

Of the smaller, known oxyanions are then only left P^3-O-P^5-O-P^3 and P^3-O-P^5-O-P^5. The first is readily hydrolyzed [W19]:

$$P^3\text{-O-}P^5\text{-O-}P^3 \rightarrow P^3\text{-O-}P^5 + P^3,$$

and in order that ^{32}P should be quantitatively transferred to P^3-O-P^5, it must sit in the centre position of the original anions. The P^3-O-P^5-O-P^5-anion is less well known, but it appears [W19] that it can also (by an unknown reaction) yield P^3-O-P^5. We therefore tentatively identify the X-anions as being these two trimers. In a few cases - especially with reactor-irradiated hypophosphites [F10] - we checked that no positive or volatile ^{32}P-labelled species (e.g. PH_3) had been formed. This was to be expected since even under the severe irradiation conditions of isotope production, there is little gas produced in phosphates [T2].

From the above it appears that we find nearly all ^{32}P-activity from neutron-activated samples in the form of oxyanions containing not more than three phosphorus atoms. Since this is not in agreement with the findings of some other authors (cf. sec. 3.2), it was on various occasions attempted to separate more species. In the experiments with solutions (cf. sec. 3.4, [F17]) it was found that the precipitated pyrophosphate sometimes contained a few per cent unidentified activity; with solid orthophosphates this was not the case.

In order to unravel the rather complex schemes of successive reactions which were observed in the following experiments, the individual yields of ^{32}P-labelled anions have been grouped, either according to skeletons, without considering the state of oxidation of the ^{32}P (cf. sect. 3.0), or according to whether ^{32}P is bonded to hydrogen ("reduced" species) or not ("oxidized" species).

3.4. The $^{31}P(n,\gamma)^{32}P$-Reaction in Solutions of Potassium Phosphate

Solid orthophosphates can contain up to twelve water molecules per phosphate ion, and aqueous solutions of phosphate ions can be made in concentrations up to about 5 M, corresponding to about eight water molecules per phosphate ion. Therefore an investigation of the chemistry of recoil-^{32}P in solutions might yield information on possible reactions in solids.

In our experiments [F17] solutions of potassium orthophosphate in various concentrations and at various pH were reactor-irradiated at ambient temperature (~ 35°C) and analysed by electrophoresis. The ^{32}P-distributions were normally fairly simple, with sharp peaks for only the five anions, P^5-O-P^5, P^3-O-P^5, P^5, P^3, and P^1 (cf. fig. 6). Only at concentrations above 0.5 M were a few per cent of the ^{32}P-activity found at the P^2-P^4 and P^4-P^4 positions.

The investigations were based on 15 min irradiations in a thermal neutron flux of about $4 \cdot 10^{12}$ n cm^{-2}s^{-1} and with a γ-dose rate of about 0.8 Mrads h^{-1}; a few preliminary experiments with other irradiation times or dose rates did not show significantly different effects.

The activity distribution as a function of pH in 0.1 M solutions is shown in fig. 7. The distribution as a function of concentration for nearly constant pH (~9) is shown in fig. 8.

Since the final chemical form of the ^{32}P might be influenced by radical species, H, OH, and e^-_{aq}, formed by radiolysis of the solvent H_2O, various scavenger experiments were performed; it was shown that a removal of OH-radicals resulted in a drastic increase in the yields of P^1 and P^3, mainly at the expense of P^5-O-P^5. The scavenger experiments apparently indicate that ^{32}P is initially in a low state of oxidation - probably not higher than +3, but this may be due to an immediate reduction of higher charged ^{32}P by H_2O. ^{32}P will hardly have a negative charge, since the electron affinity of phosphorus (0.77 eV) is lower than that of oxygen (1.47 eV); in case of P-O bond rupture the electrons will therefore tend to follow the oxygen atom. In the following we will further assume that all P-O bonds are broken, but this is not crucial for the arguments.

It is not difficult to imagine exothermic reactions between a positively charged atomic ^{32}P-ion and H_2O, H^+, or OH^- leading to formation of P^1 and P^3 e.g.:

$$P^+ + 2\ OH^- \rightarrow HO:\underset{\cdot\cdot}{\overset{\cdot\cdot}{P}}:OH^- \rightarrow O:\underset{H}{\overset{H}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{P}}}}:O^-$$

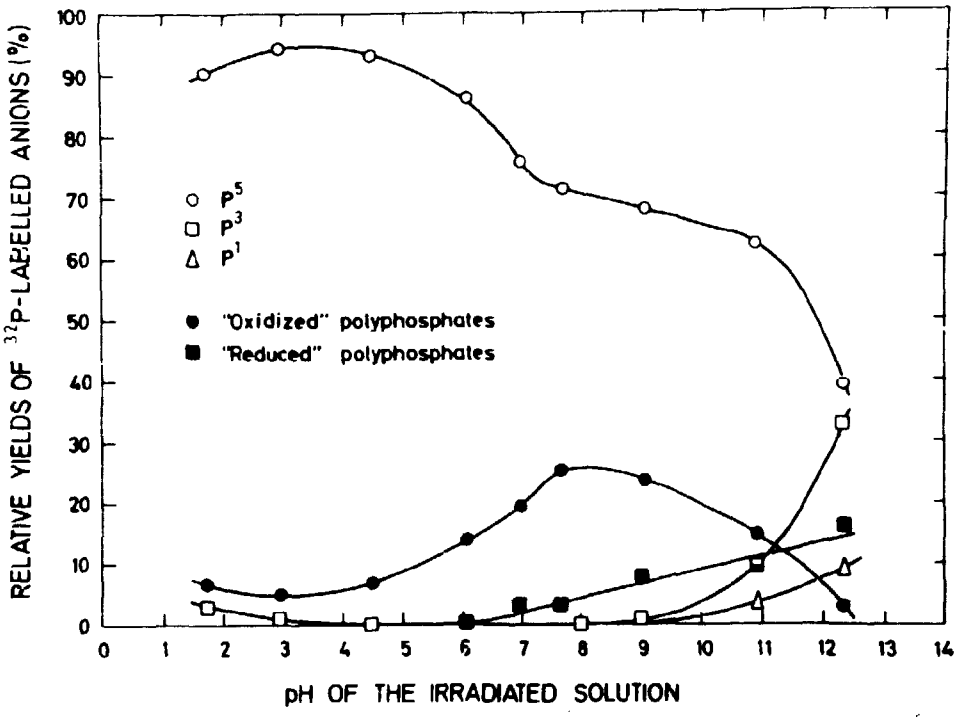


Fig. 7. The distribution of ^{32}P-activity as a function of pH in reactor-irradiated solutions containing 0.1 M orthophosphate [F17]. "Oxidized" polyphosphates represent P^5-O-P^5 with a few per cent admixture of unidentified higher polymers. "Reduced" polyphosphates represent P^3-O-P^5 and the X-anions (cf. sect. 3.3).

and:

$$P^{3+} + 3OH^- \rightarrow HO:\underset{\underset{\cdot\cdot}{H}}{\overset{\overset{H}{O}}{\overset{\cdot\cdot}{P}}}:OH \rightarrow HO:\underset{\underset{\cdot\cdot}{H}}{\overset{\overset{O}{\cdot\cdot}}{P}}:OH$$

These reactions are in agreement with the increase of P^1 and P^3 yields with pH of the irradiated solution (cf. fig. 7). An oxidation of P^3 to P^5 can further be caused by OH-radicals formed in radiolysis [H5].

It is more surprising, however, that also ^{32}P-labelled polymers - notably P^5-O-P^5- are formed. A few analyses of γ-irradiated ^{32}P-labelled solutions (cf. sect. 2.3) did not show formation of other species, therefore the neutron activation must be the initial cause.

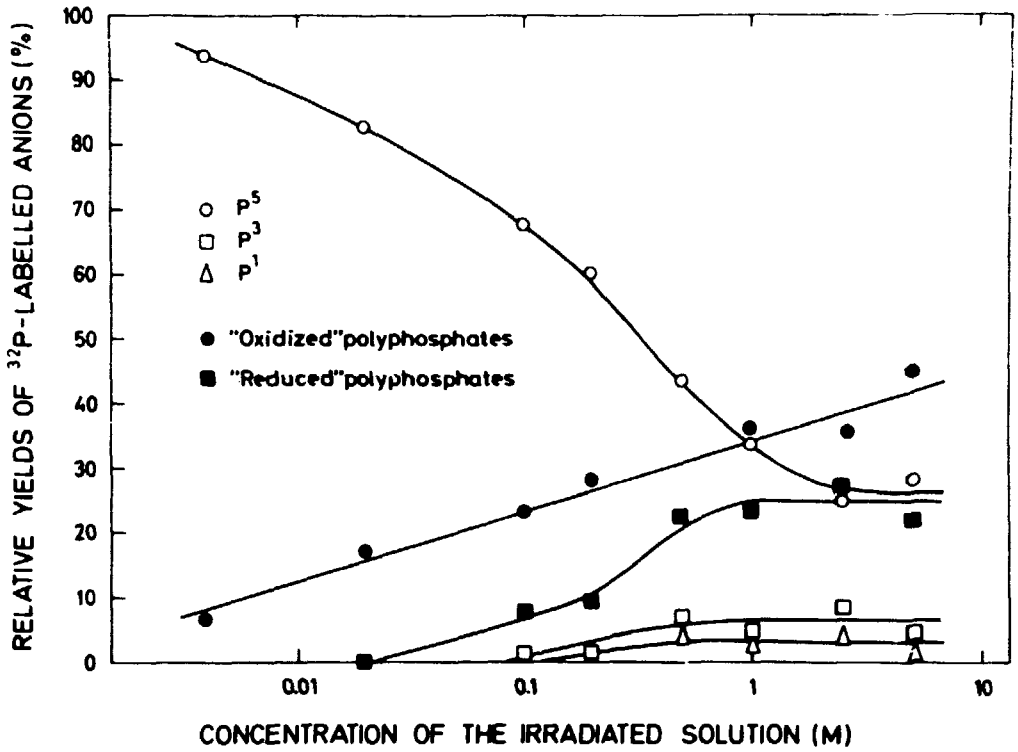
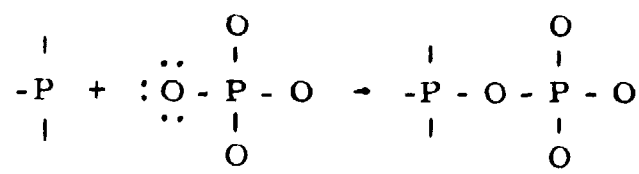


Fig. 8. The distribution of ^{32}P-activity in solutions of K_2HPO_4 (pH ~ 9) as a function of the concentration [F17]. The separation into "oxidized" and "reduced" polyphosphates is only tentative for concentrations above 0.5 M.

The slowing-down of recoiling ^{32}P in H_2O can in principle be treated as discussed in sect. 1.3, but exact calculations are not possible i.a. because the initial kinetic energy is not known. It can, however, be estimated that with the maximum energy, 1057 eV, ^{32}P is slowed down to 1 eV in less than ten collisions and to thermal energies in less than fifteen. It is therefore obvious that the formation of P-O-P bonds is possible without excess kinetic energy; thus in a 0.1 M solution the ratio between phsophate ions and water molecules is about 1:500, but the probability of P-O-P bond formation can be up to 30% (cf. fig. 8).

In order to explain the experimental results we propose the following reaction scheme: We first assume that a ^{32}P-labelled species with an electron pair vacancy - i.e. a Lewis acid - can add without activation energy to a phosphate ion:



This mechanism is in agreement with the pH-dependence of the P-O-P yield (fig. 7). For low pH the addition is prevented by protonation of the oxygen atoms; with increasing pH the yield of P-O-P increases, until at high pH the Lewis acid is neutralized with OH^- and forms monomers. The increase of P-O-P yield with the concentration of the solution (fig. 8) shows, in terms of the model, that the Lewis acid has a limited lifetime.

The OH-radicals, formed by radiolysis of water, could be important, either for the formation of the ^{32}P-labelled Lewis acid, or for a stabilization of the P-O-P bond after its formation. In other words, since formation of e.g. P^5-O-P^5 from ^{32}P in a reduced form requires both oxidation and polymerization, it is a question which process takes place first.

The first reaction ^{32}P undergoes after slowing down is probably insertion in H_2O; P^o will thus form H-P-OH. From this a Lewis acid can be formed by abstraction of an electron or a hydrogen atom. Removal of an electron cannot be accomplished by reaction with a hydroxyl radical since the ionization potential of P is higher than the electron affinity of OH. Abstraction of a hydrogen atom is exothermic with 46 kcal/mole, but addition of OH is still more favourable since the formation of a P-O bond liberates 86 kcal/mole. Therefore the effect of OH-radicals can hardly be that of producing the suggested Lewis acid from P^o.

Insertion reactions with positively charged ^{32}P will by themselves yield electron pair vacancies. Thus P^+ will form $[H\text{-}P\text{-}OH]^+$ which is an anhydrous form of hypophosphorus acid and at the same time a Lewis acid and a Brønsted acid. The rate of hydrolysis may depend on the pH, and we suggest tentatively that a neutral form H-P = O, homologous to nitroxyl H-N = O, may survive hydration long enough to react with the more nucleophilic phosphate ions. In principle a trimer can be formed in two consecutive reactions, but formation of higher polymers is not possible.

It is well known [e.g. W4] that P-O-P bonds have little or no π-bonding if one or both P-atoms are in a low state of oxidation; thus P^3-O-P^5 is hydrolyzed more easily than P^5-O-P^5 [B18]. A polyphosphate precursor of the form P^1-O-P^5 must be very unstable - especially in acidic or basic solutions. However, with OH-radicals the P^1-O-P^5 can be oxidized and thus the P-O-P bond stabilized. The increase of "reduced" polymers (P^3-O-P^5 type) at high pH may be explained by the transfer of OH into O^-:

$$OH + OH^- \rightleftharpoons O^- + H_2O$$

which is a less powerful oxidant.

In principle P-O-P bonds may also be formed in reactions between ^{32}P-labelled species with an unpaired electron and phosphate radicals, produced by OH-radicals. Although the reaction

$$HPO_4^{2-} + OH \rightarrow PO_4^{2-} + H_2O$$

has a very low rate constant ($\sim 10^6 M^{-1}s^{-1}$ [G7]) it will dominate over the reaction $2\,OH \rightarrow H_2O_2$ (rate constant $\sim 10^{10} M^{-1}s^{-1}$) for all investigated phosphate concentrations and consequently the concentration of phosphate radicals will be nearly independent of the concentration of phosphate ions. Therefore the observed concentration dependence of the P-O-P-yield suggests that polymers are not to a large extent formed in radical reactions. On the other hand the steady-state concentration of OH is controlled by the phosphate concentration, and in agreement with this we note (cf. fig. 8) a decrease of the average oxidation state of ^{32}P with phosphate concentration. These questions will be discussed in more detail in a forthcoming paper (J. Fenger and P. B. Pagsberg, to be published).

The formation of P-P bonds was found to be much less probable than reported by Kobayashi et al. [K14] for reactor-irradiated H_3PO_2, H_3PO_3, and H_3PO_4. However, their experiments were based on reactor irradiations involving γ-doses (100-300 Mrads) large enough for a macroscopic radiolysis to be detected (cf. sec. 3.2). In another work [M13] Matsuura and Lin attempted to extrapolate their results to zero γ-dose by giving reactor-irradiated solutions additional ^{60}Co-γ-irradiation; such procedures hardly lead to a correct result, since it is important that the polymer precursor is oxidized rapidly after its formation in order to avoid hydrolysis (cf. also sect. 3.6).

3.5. The $^{31}P(n,\gamma)^{32}P$-Reaction in Various Salts of Phosphorus Oxyacids

The importance of lattice parameters for the chemical effect of $^{31}P(n,\gamma)^{32}P$-reactions was investigated by comparing the ^{32}P-distributions for a series of neutron-activated alkali and ammonium salts. Fourteen orthophosphates, two phosphites, two hypophosphites, and ten salts with polymer anions were reactor-irradiated (15 min; -196°C; $4.5 \cdot 10^{12}$ n·cm^{-2}s^{-1}; 1.2 Mrads h^{-1}) and analysed immediately without further treatment.

The detailed distributions of ^{32}P-labelled anions are given in ref. F10; they are all significantly different, although similarities were observed for crystals of similar structure.

The distribution of ^{32}P over different states of oxidation appears to depend upon the amount of crystal water, the number of acid hydrogen, and upon the cation, but not upon the original state of oxidation of the ^{31}P and upon whether the parent anion is complex or monomer. In the judgment of these data it should, however, be realized that (cf. e.g. sect. 3.6) the state of oxidation of ^{32}P is to a large extent determined by γ-annealing during the reactor irradiation; therefore the effects are partly obscured by different susceptibilities to annealing of the different crystals.

More consistent information is obtained on the skeletons of the ^{32}P-labelled anions. The total yield of anions containing more than three phosphorus atoms is for none of the salts more than a few per cent; the highest yields (~7%) are observed in anhydrous phosphite and hypophosphite. Also the yields of the identified trimers, P^5-O-P^5-O-P^5 and P^4-P^4-O-P^5, are low; only in the parent compounds do they account for more than about two per cent each. The anions, assumed to be trimers with ^{32}P in a reduced state (cf. sec. 3.3), have somewhat higher yields - especially in hypophosphites and polyphosphates containing phosphorus in a reduced state (up to 19%).

In all salts with phosphorus only in oxidation states 4 and 5 the P^3-O-P^3-anion has a low yield, or is not detected at all; but in all salts containing phosphorus in lower oxidation states - i.e. phosphorus bonded to hydrogen - the yield of ^{32}P-labelled P^3-O-P^3 is higher, up to 14% for the parent compound. The yield of the anion, assumed to be P^2-P^2 exhibits the same trends.

The total yield of ^{32}P-labelled polymers does not appear to depend upon whether the parent anion is polymer or not; nor seems the original state of oxidation of the phosphorus to be important. On the other hand the total yield of polymers drastically decreases if the lattice is "diluted" with crystal water; further the fractional contribution of P-P structures to the polymer yield decreases with the amount of crystal water. This is demonstrated for orthophosphates in table 1.

The orthophosphates formally correspond to aqueous solutions with concentrations from 5 to 15 M, and a comparison between table 1 and fig. 8 shows that the total yield of ^{32}P-labelled polymers in solutions of neutron-activated crystals is very similar to the yield in neutron-activated solutions. Also low yields of polymers with more than two phosphorus atoms and rapidly decreasing yield of P-P structures with dilution are common features for the solids and the solutions.

Table 1

The total yield of ^{32}P-labelled polymers (%) and the fractional contribution from P-P structures as a function of the amount of crystal water in orthophosphates. (Average values from ref. F10)

Number of H_2O per PO_4^{3-}	0	1	2	3	4	12
Total yield of polyphosphates	74	71	62	62	57	37
P-P yield/total yield	0.17	0.11	0.11	0.11	0.10	0.7

The ^{32}P-distributions presented in ref. F10 differ from those of other authors mainly by having higher yields of "reduced" species, and higher yields of polymers. The best agreement is found with Lindner's results [L7, L8], and most of our observations agree with his hypothesis that a ^{32}P-labelled fragment (which may well be a Lewis acid, cf. sect. 3.4) is linked to one or two phosphorus-oxyanions to form a polymer. On the other hand the hypothesis implies that, in e.g. pyrophosphates, ^{32}P-labelled trimers should be formed in high yields - and this was not observed; this problem is treated further in sect. 3.7.

The formation of P-P bonds obviously cannot be a direct addition, but requires - at least in orthophosphates - removal of an oxygen atom from an inactive phosphate ion. It was shown by ESR-measurements (sect. 3.1) that heavy atoms can effectively displace oxygen to form phosphite radicals in normal lattice positions; it has also been observed that P-P bonds can be formed in Y-irradiated salts [M23] or solutions [M14] via the formation of phosphite radicals. Possibly a hot recoil ^{32}P-atom first displaces an oxygen atom and subsequently reacts with the remaining PO_3^{2-} to form a P-P bond. This would explain why the yields of P-P species decrease more rapidly than the yields of P-O-P species when the samples are "diluted" in solution and in the solid state.

In the crystals, the distance between the phosphorus-oxyanions is generally much larger than the length of P-O-P and P-P bonds (~3 and 2 Å respectively); therefore, the formation of such bonds in the solid requires that ^{32}P leave the original lattice site.

3.6. Annealing Experiments with Ammonium di-Hydrogen Phosphate

More detailed studies were made with $NH_4H_2PO_4$ [F3, F7]. The main objective was to establish whether the P-O-P bonds were present in the solid sample or were not formed until the dissolution prior to analysis; only results related to this question are discussed in detail below.

Various preliminary experiments (unpublished) did not show any significant changes of the yields of the individual anions with changes in the conditions of dissolution (temperature, pH, etc.). As a whole the results indicate that if the skeletons of the ^{32}P-labelled anions are formed upon the dissolution of the irradiated sample, the mechanisms are hardly those proposed for solutions (cf. sect. 3.4). In all the experiments described below the standard procedure (cf. sect. 3.3) was used.

In the first, and most extensive, studies with $NH_4H_2PO_4$ [F3] essentially only seven different ^{32}P-labelled anions were distinguished, in order of increasing migration: P^5-O-P^5, P^4-P^4, P^2-P^4, P^3-O-P^5, P^5, P^3, and P^1. In addition a few per cent of the ^{32}P-activity was found in the region between the P^5-O-P^5- and the P^4-P^4-peaks probably mostly as P^5-O-P^5-O-P^5

Fig. 9.shows the activity distributions obtained in analyses of samples that had been reactor-irradiated at different temperatures for a short time, but not thermally annealed afterwards. It is noted that up to about 0°C the yields of the different skeletons are nearly constant - only a slight increase in the yield of P-P species is observed. On the other hand the yield of ^{32}P in higher oxidation states drastically increases; in particular, a higher irradiation temperature results in formation of P^5-O-P^5 at the expense of P^3-O-P^5. Qualitatively the same pattern is observed [F3] if the reactor irradiation time is prolonged, or if the samples are given an additional γ-dose.

Tempering annealing experiments (cf. sect. 2.1) based on samples irradiated at various temperatures showed a different picture (cf. figs. 13.4 - 13.8 in ref. F3). The most important reaction proceeds well below 0°C; it does not change the state of oxidation of ^{32}P, but transfers ^{32}P from the P^3-O-P^5-fraction to the P^3-fraction; this shows that in P^3-O-P^5-anions, the P^3-atom contains the ^{32}P-nucleus. Similar observations were made by Claridge and Maddock [C16] and Lindner and Harbottle [L7]. It is worth noting (cf. fig. 13.8 in ref. F3) that after a slight annealing the total yield of anions with P-O-P skeletons - i. e. P^3-O-P^5 and P^5-O-P^5 - is higher in the samples that were irradiated at -78°C than in those irradiated at -196°C.

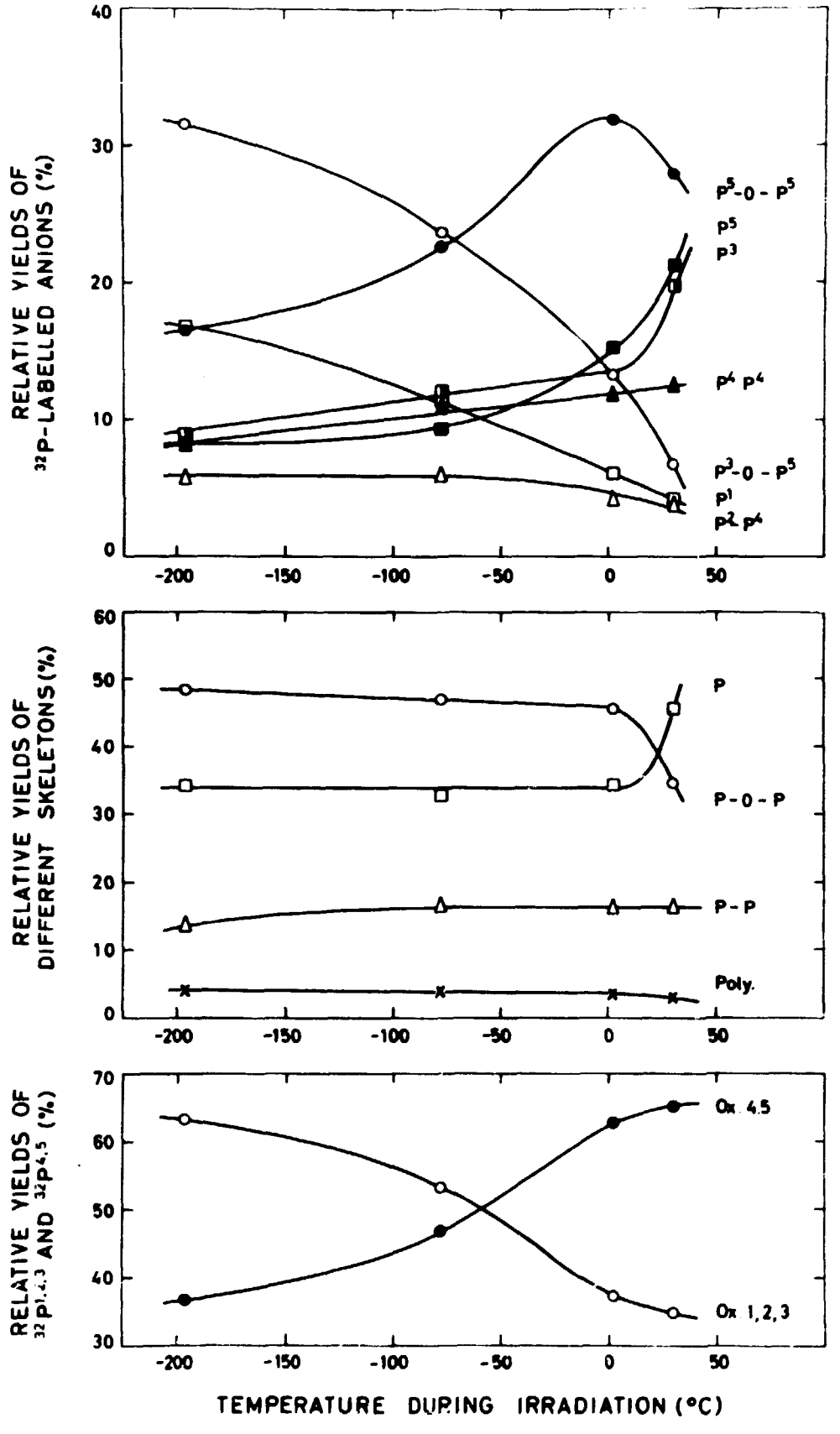


Fig. 9. The upper diagram shows the relative yields of ^{32}P-labelled phosphorus-oxyanions in activated $NH_4H_2PO_4$ as a function of the temperature during irradiation. All samples were reactor-irradiated for 24 min. Average neutron flux: $4.6 \cdot 10^{12}$ n cm^{-2}s^{-1}, and average γ-dose rate: 1 Mrad/h. A few species with low yields are not shown. In the two lower diagrams the yields of ^{32}P-labelled phosphorus-oxyanions shown above are summed according to the type of skeleton and state of oxidation. All species are included [E3].

Since the $^{32}P^3$-O-P^5 can be oxidized or degraded selectively by various treatments of the solid samples, it is reasonable to assume that its skeleton is formed in the crystal lattice and not upon dissolution. On the other hand the ^{32}P-atom may not yet have all valencies saturated, i. e. the isohypophosphate ion (cf. sect. 3.0) as such is not present in the lattice.

Baumgartner and Maddock [B13] have in a different context proposed that radiation annealing proceeds in two steps: first a removal of an electron from the radioactive fragment (formally an oxidation), then a thermal recombination or an exchange reaction. Therefore formation of electron acceptor sites at irradiation facilitates concurrent thermal annealing provided that the irradiation is performed at a high enough temperature, so that the thermal step follows close upon the radiation-induced change. If, on the other hand, the irradiation is performed at a lower temperature, the radiation-induced entity may not survive long enough, and little or no annealing results.

In our case one radiation annealing reaction may be a recombination between the P^3-end of P^3-O-P^5 and an oxygen ligand, and the proposed scheme can explain why the yield of P^5-O-P^5 increases with the irradiation temperature at the expense of P^3-O-P^5. The oxidation of the $^{32}P^3$-end to $^{32}P^5$ means a stabilization of the P-O-P bond (cf. sect. 3.3); this explains why in slightly annealed samples the total yield of remaining P-O-P species is higher if the irradiation is performed at -78°C than if the irradiation is performed at -196°C.

By a similar reasoning a discrepancy between our results and those of Claridge and Maddock [C16] can be accounted for. We observed that Y-irradiation has little effect on the distribution of ^{32}P over different skeletons, whereas Claridge and Maddock [C15] have found that radiation annealing leads to an increase in the relative yield of polymer anions. They interpreted this as radiation-induced polymerization, but there is an alternative explanation. If we assume that the samples are slightly annealed before the analyses, e. g. during the dissolution, the following reaction may have taken place:

$$^{32}P^3\text{-O-}P^5 \xrightarrow[\text{heat}]{} {}^{32}P^3 + P^5 .$$

If, however, the samples are irradiated before the analyses, then:

$$^{32}P^3\text{-O-}P^5 \xrightarrow[\text{radiation}]{} {}^{32}P^5\text{-O-}P^5 ,$$

which is more stable; therefore apparently:

$$^{32}P^{3} + P^{5} \xrightarrow[\text{radiation}]{} {}^{32}P^{5}\text{-O-}P^{5}.$$

The formation of P-P species was in sect. 3.5 proposed to proceed via the formation of PO_3^{2-}-radicals. Recoil fragments, which can add to a PO_4^{3-}-ion, will form less stable species if they react with a PO_3^{2-}-radical on the empty oxygen site; this explains why the yield of P-P species increases slightly with irradiation temperature (cf. fig. 9) and additional γ-dose [F3].

The observation of a marked effect of the temperature at which the $NH_4H_2PO_4$-samples were neutron-activated, and of a high susceptibility to thermal and radiation annealing demonstrated that the distributions of ^{32}P-activity discussed above might not represent the best possible approximation to the situation in the crystal. In a new study [F7], a series of analyses was performed on samples that were irradiated at -196°C for periods down to 5 seconds and dissolved at 0°C within a few minutes after pile-out.

Now the yield of the P^3-O-P^5 was reduced, and a corresponding amount of unidentified activity was found on both sides of the P^5-peak (the X- and Y-species discussed in sect. 3.3). It was also found that the retention (P^5) was only about 6% - i.e. lower than indicated in fig. 9. These new species proved to be so unstable in the solid samples that controlled annealing studies were impossible.

If the X-species - as proposed in sect. 3.3 - are trimers with ^{32}P in a reduced state, we have an alternative explanation of the high yield of tripolyphosphate found by e.g. Lindner [L8] (cf. sect. 3.2). In those experiments the samples were presumably irradiated in a facility with a larger γ-dose rate than in our case (cf. sect. 2.1), and consequently the X-species could have been stabilized by oxidation in analogy with the stabilization by oxidation of the P-O-P bond in P^3-O-P^5.

3.7. Annealing Studies with Potassium Pyrophosphate

The low yield of ^{32}P-labelled anions with more than two phosphorus atoms found in reactor-irradiated salts with polymer anions (cf. sect. 3.5) called for a closer investigation. For this purpose was chosen anhydrous potassium

pyrophosphate, $K_4P_2O_7$ [F13], which had shown [F10] a high yield of polymers.

The thermal annealing of ^{32}P-recoil species was investigated in a tempering experiment similar to the one performed on $NH_4H_2PO_4$ (cf. sect. 3.6), and it appears that the two compounds exhibit analogous annealing reactions for ^{32}P. In the orthophosphate $^{32}P^3$-O-P^5 is formed as a consequence of an (n, γ)-reaction, the P-O-P bond is easily broken down by thermal annealing, and the resulting $^{32}P^3$ is then fairly stable in the lattice. In the pyrophosphate a significant amount (about 13%) of the ^{32}P-activity is found in anions with three or more phosphorus atoms - notably in the unidentified X-species (cf. sect. 3.3). These higher polymers are decomposed to P-O-P species even at dry-ice temperature, and the resulting P^3-O-P^5 is stable up to about 100°C.

The conclusion, therefore, is that the formation of P-O-P bonds by addition of a ^{32}P-labelled fragment to an anion in a pyrophosphate lattice is quite probable, but that the products are so unstable that they may not be detected. This explanation, however, is not quite satisfactory, since an addition-reaction involving e.g. $^{32}P^3$:

$$^{32}P^3 + P^5\text{-O-}P^5 \rightarrow {}^{32}P^3\text{-O-}P^5\text{-O-}P^5$$

would presumably give a species that would break at the bond between P^3 and P^5 to give $^{32}P^3$ and not the observed ^{32}P-labelled P^3-O-P^5. On the other hand, the electronic structure of these species is not known, and it has been observed [W19] that in solution P^3-O-P^5-O-P^5 may decompose and yield P^3-O-P^5. It is also interesting to note (cf. fig. 2 in ref. F13) that the P-O-P species that are formed in annealing reactions below 0°C are apparently degraded to monomers above 0°C before the ^{32}P finally returns to the parent P^5-O-P^5. One might therefore imagine that these intermediate ^{32}P-labelled species are not situated in regular lattice positions.

3.8. Conclusions Drawn from the "Phosphorus Experiments"

The above-described experiments with $^{31}P(n, \gamma)^{32}P$-reactions in phosphorus-oxyanions form a conventional "hot-atom study" of a chemical system, which has been investigated before. However, the experiments were made under more favourable reactor irradiation conditions and with a refined analytical technique; consequently the results are more accurate than - and in some respects significantly different from - those published previously.

Our results indicate that ^{32}P immediately after the (n, Y)-reaction has a low state of oxidation (~+1); subsequently it may be found in higher states of oxidation and possibly as part of a polymer anion. Experiments with solutions (sect. 3.4) show that the formation of a ^{32}P-O-P bond can take place in a thermal reaction between a reduced ^{32}P-labelled species and an inactive phosphate ion; possibly the ^{32}P has an electron pair vacancy and is simply added to a lone pair of electrons on an oxygen atom. Two consecutive addition processes can lead to a trimer, but higher polymers can hardly be formed. After the formation of the skeleton of the anion, the ^{32}P is oxidized to P^{3}- or P^{5}-, whereby the P-O-P bond becomes sufficiently stable to be observed analytically.

Experiments with solids (sects. 3.5-3.7) give analogous results; the yields of polymer anions are higher, but only anions with 2 or 3 phosphorus atoms are formed in significant amounts. The skeletons of these anions are formed in the solid samples, and this requires that the ^{32}P leave the original lattice site; since total polymer yields of nearly 80% are observed in anhydrous crystals, this must be a very probable result of the (n, Y)-recoil. The formation of P-P bonds in orthophosphates requires that first a P-O bond in an inactive PO_4^{3-}-ion is broken to form a phosphite radical, PO_3^{2-}. This bond-breaking requires energy, which can be supplied from the recoiling atom. However, we are not able to establish whether the P-P bond formation itself is a hot reaction; possibly the ^{32}P-atom is stopped in the vicinity of the PO_3^{2-}-radical and subsequently reacts with it thermally.

The final state of oxidation of the ^{32}P is not much dependent upon the original state of the ^{31}P; this is consistent with the assumption that in the recoil process ^{32}P breaks all bonds to the ligands. Unfortunately, however, the oxidation state is so strongly influenced by other factors (cf. sects. 3.5 and 3.6) that no definite conclusions can be drawn.

The results summarized above are in agreement with Lindner's earlier results [L7, L8], but give a more detailed picture of the recoil event. This event seems to be reasonably well described by Bunker and Volkenburgh's model experiments (cf. sect. 3.2 and ref. B27). Formation of higher polymers could have taken place if a large amount of inactive molecular fragments (e.g. PO_3^{2-}) were formed. In contradistinction to Anselmo [A17, A18] and Nakamura et al. [N1] we did not observe these polymers, and must therefore conclude that the $^{31}P(n, Y)^{32}P$-reaction does not cause much damage to the crystal lattice.

The ESR-measurements (sec. 3.1) do not give full information on the radiolysis of phosphorus oxyanions since only species with unpaired electron

spins are detected, but it appears that the displacement of a central atom is a very unlikely process. A movement of a whole HPO_2^--radical has been observed in a single case, but under such conditions that this effect cannot in general account for the formation of polymers. We must therefore conclude that in phosphates the chemical effects of (n, γ)-reactions cannot be fully explained on the basis of known radiolytic effects. In contradistinction to other authors we believe that the main effect of γ-radiation is not to form polymers but to stabilize them.

Formation of polymer anions has been indicated in various systems [e.g. A13], but never in such stable forms and with such high yields as in the phosphate system. Maddock and Collins [M5], however, have suggested that (op. cit.) "the unusual feature of the phosphate system is not that polynuclear species are formed, but that they are stable upon solution of the irradiated salt in water". They further expect that (op. cit.) "the radioactive polynuclear products may play a very important part in annealing processes. Such processes will arise from either, or both, a redox reaction affecting the polynuclear complex and/or a rearrangement of ligand units within the complex".

Our findings can only partly support this hypothesis, since it seems that, in some annealing reactions, oxidation and degradation can proceed independently. Possibly the P-O-P bond can act as a means of electron transfer in the oxidation of e.g. $^{32}P^1$-O-P^5, but the instability of the hypothetical P^1-O-P^5-anion has so far prevented a closer investigation.

4. REACTIONS IN IRON COMPOUNDS

I. RADIOCHEMICAL ANALYSES

Natural iron contains four stable isotopes ^{54}Fe (5.8%), ^{56}Fe (91.7%), ^{57}Fe (2.2%), and ^{58}Fe (0.3%); neutron activation produces the radioactive ^{55}Fe and ^{59}Fe. ^{55}Fe, which decays by electron capture with a half life of 2.7 years, is difficult to trace in radiochemical analysis and has apparently never been used systematically in hot-atom chemistry. The chemical effects of the $^{58}Fe(n, \gamma)^{59}Fe$-reaction (fig. 10) havebeen used for preparation of ^{59}Fe of high specific activity, [e.g. K7]. The maximum γ-recoil energy is 394 eV, but the decay scheme is not known sufficiently well for a detailed calculation of the γ-recoil distribution; it appears, however, that there are no converted transitions [K13]. Ground-state ^{59}Fe decays by β-γ-emission with a half life of 45 days and can be measured quantitatively without inter-

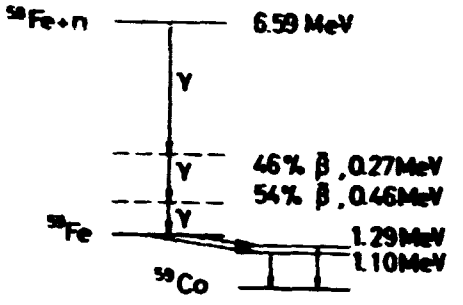


Fig. 10. The $^{58}Fe(n,\gamma)^{59}Fe$-reaction.

ference from ^{55}Fe. The activation cross section for ^{58}Fe is about 1 b, but because of the low natural abundance (0.3%), long reactor irradiations are necessary to produce sufficient activity for radiochemical analysis, and this is unfortunate since some iron compounds are very sensitive to radiolysis (cf. fig. 3 p. 25). This effect can of course be reduced by using samples enriched in ^{58}Fe, but this has apparently not been done in any of the experiments described by others.

The physics and chemistry of iron make it an attractive element for two types of hot-atom studies:

(1). Iron forms compounds with two different iron sites; further the stable isotope ^{58}Fe is activated by neutron capture, whereas the stable isotope ^{56}Fe is not. Pairs of samples prepared with one of the sites enriched in ^{56}Fe and the other in ^{58}Fe therefore permit studies of the importance of the original chemical form of the recoil nucleus for its final fate. Such experiments are discribed in sects. 4.2 and 4.3.

(2). Iron is a convenient Mössbauer nucleus, which can be formed in various nuclear reactions; this permits comparisons to be made between chemical effects of different reactions and between results obtained with different experimental techniques. For studies of chemical effects of the $^{57}Co(EC)^{57}Fe$-reaction it is important that cobalt and iron form analogous compounds. Mössbauer experiments are treated separately in chapter 5.

Radiochemical analysis of iron compounds poses a problem that is not met in e.g. phosphorus studies. In solids, iron appears as "free" Fe^{2+} and Fe^{3+} as well as ferrous and ferric complexes, which may be present simultaneously in the samples; however, when the solid is dissolved in

water, electron exchange between Fe^{II}- and Fe^{III}-species is greatly facilitated. In ordinary analytical chemistry these exchange reactions can be ignored, and e.g. Fe^{2+} and Fe^{3+} can readily be determined in the presence of each other. When, however, e.g. solid ferrous sulphate (cf. sect. 4.1) containing "carrier-free" $^{59}Fe^{3+}$ is dissolved in water prior to radiochemical analysis, the ^{59}Fe will be statistically distributed between Fe^{2+} and Fe^{3+}; i.e. it is almost completely transferred to the Fe^{2+}-fraction. "Carrier-free", labelled complexes, e.g. $^{59}Fe(CN)_6^{3-}$ in salts containing $Fe(CN)_6^{4-}$, may have a similar fate.

We found that a disturbing electron exchange can be effectively quenched by dissolving the samples in the presence of a strong complexing agent e.g. αα'-dipyridyl [S19], but by so doing weaker complexes can be broken down, and consequently information on the structure of ^{59}Fe-labelled species is lost. On the other hand, if the exchange is ignored, only information on structure is obtained. These, and similar problems are discussed further in sects. 4.1-4.3.

4.1. The $^{58}Fe(n,\gamma)^{59}Fe$-Reaction in Ferrous Sulphate and Iron Oxalates

Our first studies of the chemical effects of the $^{58}Fe(n,\gamma)^{59}Fe$-reaction in simple salts were made with ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and ferrous oxalate ($FeC_2O_4 \cdot 2H_2O$) [F8]. Later also ferric oxalate ($Fe_2(C_2O_4)_3 \cdot xH_2O$) and potassium trisoxalatoferrate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$) were investigated [S20]. These compounds were chosen because they are suited for parallel Mössbauer studies (cf. sects. 5.2 and 5.3). Since it is easy to distinguish between $^{57}Fe^{II}$ and $^{57}Fe^{III}$ in Mössbauer spectra of iron oxalates, it was decided to concentrate on the determination of the state of oxidation of the recoil-^{59}Fe.

The analytical procedure [S19] was nearly the same for all the compounds. The neutron-irradiated samples were dissolved in the presence of αα'-dipyridyl, which forms the $Fe(dipy)_3^{2+}$-complex with Fe^{II}; then Fe^{III} was precipitated as $Fe(OH)_3$ [S24]. The relative yields of $^{59}Fe^{II}$ and $^{59}Fe^{III}$ were determined by measurements of the γ-activity in the supernatant and precipitate respectively. This method was tested on material labelled with ^{59}Fe, and it turned out that in all cases a small amount of activity was found in the wrong fraction. In the ferrous salts this is probably due to a small content of Fe^{III} (0.6% in $FeC_2O_4 \cdot 2H_2O$; 2% in $FeSO_4 \cdot 7H_2O$) [S19]. In analyses of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$, however, about 5% of the ^{59}Fe-activity was found as Fe^{II}, whereas Mössbauer analyses demonstrated

that the solid samples contain at most 2% Fe^{II}. Apparently Fe^{III} in the $Fe(C_2O_4)_3^{-3}$-ion is slowly reduced in aqueous solution [S20], probably by a photochemical reaction [B6]. Analyses of labelled $Fe_2(C_2O_4)_3 \cdot xH_2O$ gave about 5% $^{59}Fe^{II}$.

Labelled material was also used in investigations of the radiation and thermal stability of the oxalates which were given a γ-dose or a thermal treatment before the analyses. In agreement with previous investigations [e.g. S35] $Fe(C_2O_4) \cdot 2H_2O$ was found to be stable against γ-induced oxidation, whereas $Fe_2(C_2O_4)_3 \cdot xH_2O$ [S2] and $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ [e.g. B9] were found to be very sensitive to γ-induced reduction (G ~10 and 7 respectively).

Both the systematic error in the analyses and a possible macroscopic decomposition must be taken into account in the interpretation of the experimental results. An example is shown in sect. 2.3, fig. 3.

The distribution of recoil ^{59}Fe over Fe^{II} and Fe^{III} was determined immediately after reactor irradiation for 1 hour at various temperatures. The relative yields of foreign valency states were for irradiations at -196°C and after correction for macroscopic effects:

$^{59}Fe^{III}$ in $Fe^{II}SO_4 \cdot 7H_2O$: ~2%

$^{59}Fe^{III}$ in $Fe^{II}C_2O_4 \cdot 2H_2O$: $9 \pm 0.5\%$

$^{59}Fe^{II}$ in $Fe_2^{III}(C_2O_4)_3 \cdot xH_2O$: 3 ± 1 7

$^{59}Fe^{II}$ in $K_3Fe^{III}(C_2O_4)_3 \cdot 3H_2O$: $60 \pm 3\%$.

The small amount of $^{59}Fe^{III}$ in $FeSO_4 \cdot 7H_2O$ was only observed if the analyses were performed at 0°C; it completely disappeared when the samples were handled and dissolved at room temperature. Apparently a rapid annealing takes place, and the initial yield of $^{59}Fe^{III}$ may thus be significantly higher than 2%. The yields of foreign valency iron in the three oxalates were the same for irradiation at -196°C and -78°C, but were reduced at higher temperatures. After irradiation at reactor temperature (30-40°) the yields of $^{59}Fe^{II}$ in the two Fe^{III}-oxalates were so low that they could almost be accounted for by the macroscopic effects only. The influence of thermal annealing on the distribution of recoil-^{59}Fe over Fe^{II} and Fe^{III} was investigated in tempering experiments (cf. sect. 2.1). In the two Fe^{III}-oxalates all recoil-$^{59}Fe^{II}$ was annealed to $^{59}Fe^{III}$ at 45°C. In $FeC_2O_4 \cdot 2H_2O$ the annealing of $^{59}Fe^{III}$ to $^{59}Fe^{II}$ started at 45°C and had

not been completed at 120°C (above 120°C the salt is decomposed). The $^{59}Fe^{III}$ in $FeC_2O_4 \cdot 2H_2O$ could also be annealed by modest UV-irradiation at 25°C, suggesting that electronic excitations were involved. On the other hand, it was shown that there was no correlation between the annealing and the emission of thermoluminescence; these effects were not further investigated.

Although the underlying mechanisms are not fully understood, the results for the three oxalates show that in these systems (n, γ)-reaction and γ-radiolysis do not have the same effects. In ferrous oxalate the mechanical recoil can cause oxidation of the recoiling ^{59}Fe, but the compound as such is extremely stable against radiolysis [S35]. In ferric oxalate, on the other hand, the mechanical recoil has a strikingly low probability of changing the state of oxidation of the recoiling ^{59}Fe, but the compound is very unstable towards γ-induced reduction [S35].

In potassium trisoxalatoferrate a substantial amount of the ^{59}Fe is found as $^{59}Fe^{II}$, but the $^{59}Fe^{II}$ is much more rapidly annealed than the Fe^{II}-species formed in radiolysis (cf. sect. 5.3 and ref. B 9). With the analogous compound $K_3Co(C_2O_4)_3 \cdot 3H_2O$ Shankar et al. [S15] found that $^{59}Co(n,\gamma)^{60}Co$-reactions produce only $^{60}Co^{2+}$ and $Co(C_2O_4)_3^{3-}$; dissolution of the irradiated samples in the presence of $C_2O_4^{2-}$ did not give any change in the yield of $Co(C_2O_4)_3^{3-}$, indicating that no unstable ligand-deficient species - e.g. $Co(C_2O_4)_2^-$ - were formed. This suggests that our $^{59}Fe^{II}$-fraction is in fact $^{59}Fe^{2+}$ and not a weak oxalato complex (cf. sect. 4.0).

The potassium trisoxalatoferrate system has been extensively studied by Caluşaru and Rusi [C1, C2, R9], who have presented results significantly different from ours. It appears, however, that during the neutron activation Calusaru and Rusi's samples have received more than 1000 Mrad γ-radiation; therefore, what they have observed undoubtedly results from a macroscopic γ-radiolysis (cf. sect. 5.3).

4.2. The $^{58}Fe(n,\gamma)^{59}Fe$-Reaction in Soluble Prussian Blue and Potassium Ferrous Cyanide

As stated above (sect. 4.0) it is possible to study the chemical effects of $^{58}Fe(n,\gamma)^{59}Fe$-reactions taking place at different sites in some special iron compounds; among these, soluble Prussian blue, $KFe^{III}[Fe^{II}(CN)_6] \cdot H_2O$ [C9], is the simplest. This compound can be prepared by precipitation of either Fe^{3+} and $Fe(CN)_6^{4-}$ or Fe^{2+} and $Fe(CN)_6^{3-}$. In the solid, iron ions and hexacyanide complexes are arranged in a NaCl-structure

(fig. 11, [K6]) with K^+ and H_2O occupying alternate cubic cells [P3].

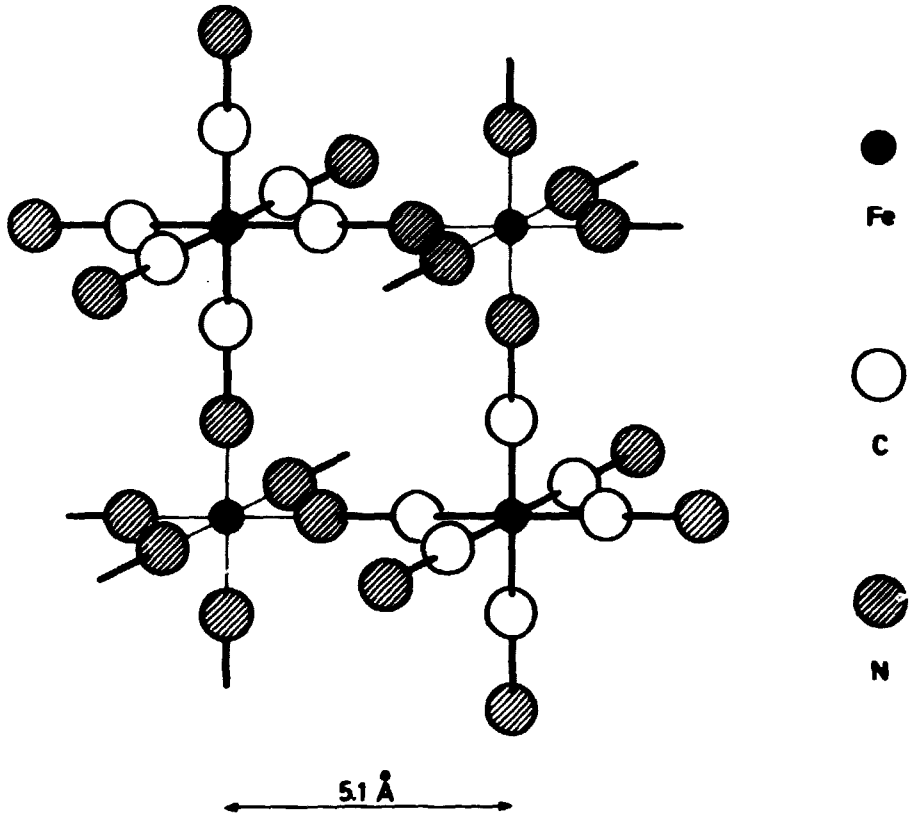


Fig. 11. Simplified crystal structure of soluble Prussian blue.

Mössbauer spectra [M8] show that the two iron atoms are present in the form of Fe^{3+} and $Fe(CN)_6^{4-}$. In spite of its name, $KFe[Fe(CN)_6]\cdot H_2O$ is not soluble, but it can form a colloidal aqueous suspension. When OH^- is added, $Fe(OH)_3$ precipitates, and $Fe(CN)_6^{4-}$ stays in the supernatant. If the uncomplexed iron used in the preparation is labelled with ^{59}Fe, all the ^{59}Fe-activity is found in the precipitated $Fe(OH)_3$; if, on the other hand, the complex is labelled, all the ^{59}Fe-activity stays in the supernatant [R4]. Only under the influence of light and in the presence of catalysts [H2] or by prolonged heating [K17] has an isotope exchange between "free" and complexed iron been observed. These observations were confirmed [F12], and it was further checked that the labelled material is sufficiently stable against γ-radiolysis and heating (*cf.* sect. 2.3). After these control experiments two different batches of $KFe[Fe(CN)_6]\cdot H_2O$ were prepared. In one batch the cation was pure ^{56}Fe, and the complex was enriched in ^{58}Fe;

in the other batch the isotopes were interchanged. In addition $K_4{}^{58}Fe(CN)_6 \cdot 3H_2O$ was prepared.

Samples from the three preparations were reactor-irradiated at various temperatures and analysed as in the control experiments. Thus only two fractions were obtained: complexed and uncomplexed iron; the results are shown in fig. 12.

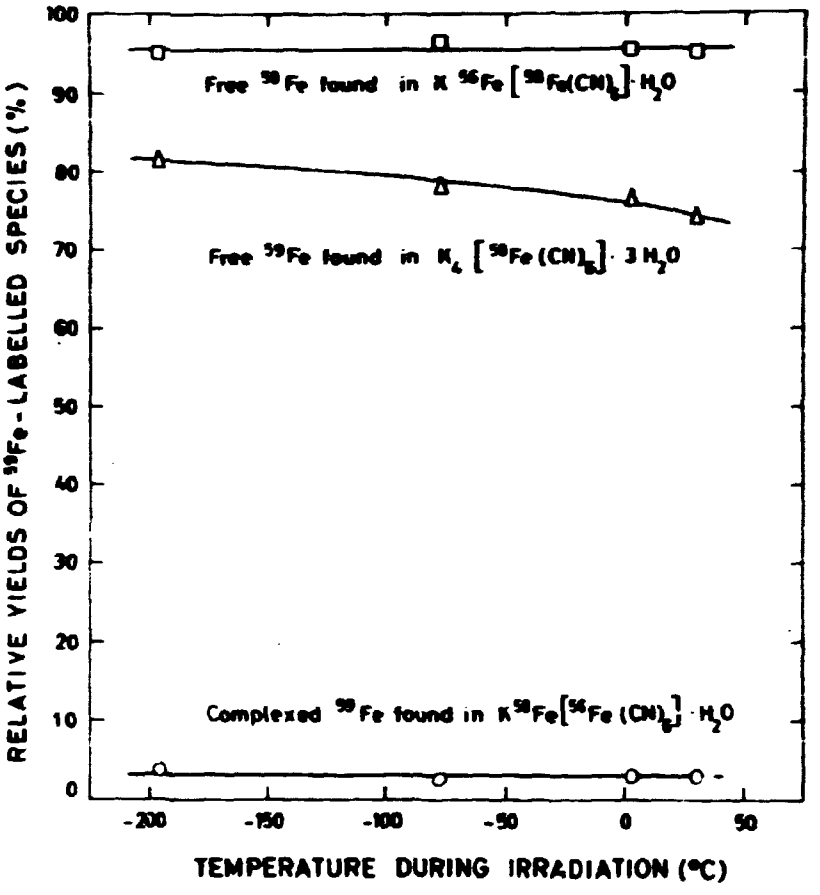


Fig. 12. The relative distribution of ^{59}Fe-activity in activated $K^{56}Fe[^{58}Fe(CN)_6]\cdot H_2O$, $K^{58}Fe[^{56}Fe(CN)_6]\cdot H_2O$, and $K_4[^{58}Fe(CN)_6]\cdot 3H_2O$ as a function of the temperature during irradiation. All samples were irradiated for 15 min. Average neutron flux: $4.6\cdot 10^{12}$ n cm^{-2}s^{-1}, and average γ-dose rate: 1 Mrad/h. [F12].

The ^{59}Fe formed in ferrohexacyanide behaves as is normally observed in recoil studies: the yield of ^{59}Fe in the parent form increases with the irradiation temperature (fig. 12) and was also found to increase upon thermal treatment. The complex fraction, which comprises not only a hexacyanide retention but possibly also pentacyanides, is without annealing 20%; this is

much less than observed in other studies [e.g. M16], but definitely more than can be accounted for by "non-bond rupture" (cf. sects. 1.3 and 1.5).

The observations with Prussian blue are completely different. The yield of ^{59}Fe that has been transferred from a cationic site to a complex in $K^{58}Fe[^{56}Fe(CN)_6]\cdot H_2O$ is only 3% - irrespective of the temperature during the irradiation. The yield of ^{59}Fe that has apparently recoiled out of a complex site in $K^{56}Fe[^{58}Fe(CN)_6]\cdot H_2O$ is 95.5% - also independent of the temperature. Consequently the sum of the yields of ^{59}Fe-labelled complexes due to (1) non-bond rupture, (2) immediate recombination with the original ligands, and (3) formation of the complex with new ligands, is 4.5%. If we assume that the probability of formation of the complex with new ligands is independent of the origin of the ^{59}Fe, it appears that the probability of non-bond rupture and/or immediate recombination is only 1.5% (4.5-3%).

In $K_4Fe(CN)_6\cdot 3H_2O$ the sum of non-bond rupture and immediate recombination must be of the order of 17% or about 10 times as high as in Prussian blue. We can only explain this by assuming that when ^{59}Fe has recoiled out of a $Fe(CN)_6^{4-}$ complex in Prussian blue, it must compete with the inactive Fe^{3+}-ions in the lattice for a recombination with the CN-ligands. A complex site (cf. fig. 13) has 6 nearest Fe^{3+} neighbours at a distance of 5.1 Å and 8 next nearest at about 9 Å ($5.1\cdot\sqrt{3}$); therefore the recoiling ^{59}Fe must at least have a range of 5-10 Å.

The above-described experiments are discussed further at the end of the next section (sect. 4.3).

4.3. The $^{58}Fe(n,\gamma)^{59}Fe$-Reaction in an Iron "Double Complex"

"Double Complexes", in which the same element is present in two different complexes, have previously been reported for some transition metals, including iron [S3], but for various reasons they were not well suited for hot-atom studies.

However, Poluektov and Nazarenko [P10] and later Markunas [M11] have observed that the ferrodipyridyl and ferrophenantroline complexes form red crystalline precipitates with ferricyanide; these precipitates had apparently never been investigated, but we showed in a series of analyses [F14, S21] that they are well-defined compounds with the formula:

$$[Fe^{II}(\begin{smallmatrix}\text{dipy}\\\text{phen}\end{smallmatrix}\text{ or})_3]_2[Fe^{III}(CN)_6]_3\cdot 1\text{-}3H_2O\,.$$

The dipy/CN combination was investigated in more detail by control experiments similar to the ones performed on Prussian blue (cf. sects. 2.3 and 4.2). No disturbing isotope exchange was observed in the solid or in aqueous solution, but the thermal stability was found to be low, dehydration starts at about 50°C and macroscopic decomposition below 100°C. Unfortunately the solubility in water is only about 1 mg/ml, but it can be increased by addition of DMSO (dimethylsulphoxide).

This double complex was prepared with two specific isotope enrichments. Then samples were reactor-irradiated at dry-ice temperature, stepwise annealed (cf. sect. 2.1), and finally analysed by high voltage electrophoresis (cf. sect. 2.2).

In the first experiments [S22a] the samples were dissolved in water. A remarkably large and irreproducible fraction (~70%) of the ^{59}Fe-activity was found in the form of $Fe(dipy)_3^{2+}$. Various experiments showed that some of this $^{59}Fe(dipy)_3^{2+}$ must have been formed during the dissolution of the samples; this suggests that free dipyridyl is formed in the samples during the reactor irradiation - possibly by bulk radiolysis - and reacts with free $^{59}Fe^{2+}$ formed in recoil reactions.

We considered scavenging of the free dipyridyl by dissolving the irradiated samples in the presence of a divalent metal cation. Such a method had been used successfully in a study of $^{59}Co(n,\gamma)^{60}Co$ reactions in solutions of trisacetylacetonate cobalt(III) [T5] and in solid tris(nitrosonaphtholato) cobalt(III) [T6]. However, no suitable cation that would not precipitate with $Fe(CN)_6^{3-}$ could be found.

In the next experiments [S22b] the samples were therefore dissolved in the presence of EDTA. The stability constant for $Fe(dipy)_3^{2+}$ [e.g. B16] is two orders of magnitude higher than for $Fe^{II}(EDTA)^{2-}$, but the concentration of free dipyridyl must be minute since EDTA in a concentration of $5 \cdot 10^{-4}$M appeared to scavenge all $^{59}Fe^{2+}$. The yield of $^{59}Fe(dipy)^{2+}$ was now reduced to about 20%, demonstrating that a secondary process had actually been suppressed.

This method has two disadvantages: (1) $^{59}Fe^{3+}$, which might be present, is immediately complexed to $^{59}Fe^{III}(EDTA)^-$ and the $^{59}Fe^{II}(EDTA)^{2-}$ complex is readily oxidized to $^{59}Fe^{III}(EDTA)^-$; therefore information on the original state of oxidation of the ^{59}Fe is lost (cf. sect. 4.0). (2) Even with optimal experimental conditions (cf. ref. S22b) $Fe(dipy)_3^{2+}$ can be decomposed by EDTA. Control experiments demonstrated that in the neutron-irradiated samples the yield of $^{59}Fe(dipy)_3^{2+}$ is measured a few per cent too low and the yield of "free" ^{59}Fe (in the form of $^{59}Fe(EDTA)^-$) correspondingly too high.

The electrophoretic separations were performed in an acetate buffer and yielded six ^{59}Fe-labelled fractions. Three were conclusively identified as $^{59}Fe(dipy)_3^{2+}$, $^{59}Fe(EDTA)^-$(corresponding to free $^{59}Fe^{2+}$ and $^{59}Fe^{3+}$), and $^{59}Fe(CN)_6^{3-}$. One fraction probably contains $Fe(CN)_5H_2O^{3-}$ and/or $Fe(CN)_5H_2O^{2-}$, and the remaining two are supposed to contain various other iron-cyano complexes with less than six CN-ligands.

The result of an annealing experiment is presented in fig. 13; only the

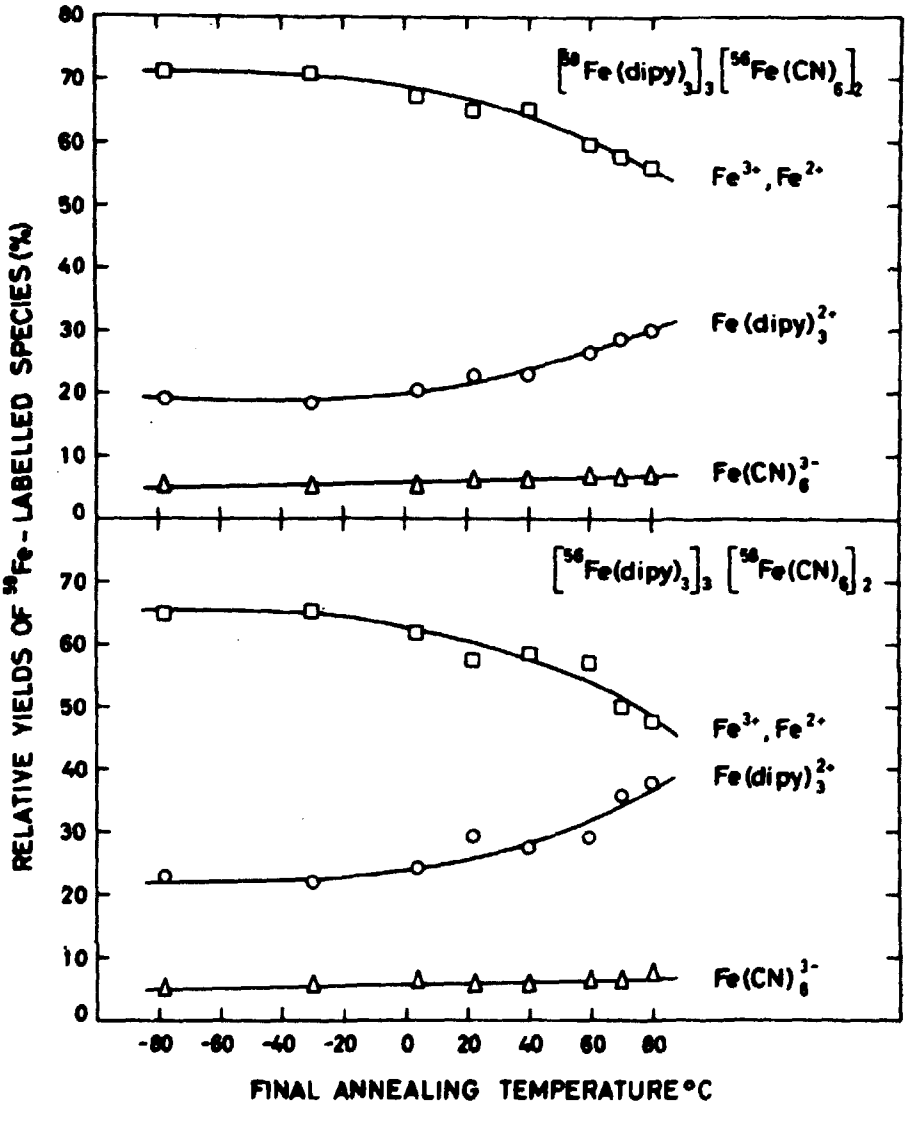


Fig. 13. The relative yields of ^{59}Fe-labelled species in activated and stepwise annealed $[Fe(dipy)_3]_3[Fe(CN)_6]_2 \cdot xH_2O$. Series of samples were reactor-irradiated for 5.8 h at -78°C ($4.5 \cdot 10^{12}$n cm^{-2}s^{-1}, 0.8 Mrads/h, then stored for 24 h at each indicated temperature, dissolved in 25% DMSO containing $5 \cdot 10^{-4}$M EDTA, and analysed by electrophoresis. (Only identified fractions are shown). [S22b].

three major fractions are plotted; the minor fractions have yields of about 2% for the samples enriched with ^{58}Fe in the dipyridyl complex, and about 2.5% for the samples enriched in the hexacyanide complex; these yields did not change significantly upon annealing.

It appears that the chemical fate of recoil-^{59}Fe depends little upon the original chemical state of the ^{58}Fe. This indicates, in agreement with the Prussian blue experiments (cf. sect. 4.2), that not only does most of the ^{59}Fe break all bonds to ligands, but it also moves sufficiently away from the lattice site to avoid immediate recombination with the original ligands.

The yields of $^{59}Fe(CN)_6^{3-}$ are the same for the two differently enriched double complexes; therefore the true retention in a ferricyanide complex must be very low. On the other hand, the total yield of the species assumed to be CN-deficient complexes is higher (~1.5%) in $[^{56}Fe(dipy)_3]_3[^{58}Fe(CN)_6]_2$ than in $[^{58}Fe(DIPY)_3]_3[^{56}Fe(CN)_6]_2$; presumably these 1.5% represent ^{59}Fe which remains in the lattice positions, but loses one or a few CN-ligands. The same may apply to the ferrocyanide complex in Prussian blue, since the analysis described in section 4.2 did not distinguish between various ^{59}Fe-labelled complexes.

The yields of $^{59}Fe(CN)_6^{3-}$ (~6%) are significantly higher than found in Prussian blue, where the complex fraction (fig. 12) may even include pentacyanides. This suggests that ^{59}Fe can hit and dissociate an inactive hexacyanide ion and subsequently react with the liberated CN-ligands. In Prussian blue, ^{59}Fe must compete with Fe^{3+} ions from the lattice, therefore the yield is reduced.

The crystal structure of the double complex is not known, but since the radius of the $Fe(dipy)_3^{2+}$-complex is about 5 Å and the radius of $Fe(CN)_6^{3-}$ about 4 Å, the distance between different iron sites must be of the order of 10 Å. Therefore recoil-^{59}Fe starting from a $Fe(dipy)_3^{2+}$-complex must have at least that range. On the other hand the range is hardly much larger, because the yield of $^{59}Fe(dipy)_3^{2+}$ is somewhat higher when ^{59}Fe starts from $Fe(CN)_6^{3-}$ than when it starts from $Fe(dipy)_3^{2+}$; this indicates a preference for reactions with the nearest neighbours.

Saito et al. [S1] investigated the chemical effects of $^{59}Co(n,\gamma)^{60}Co$-reactions in $[Co(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Fe(CN)_6]$. Although an exact distinction between recoils from the two different sites is not possible with this pair of compounds, the data indicate the same preference. Thus the yield of $^{60}Co(NH_3)_6^{3+}$ is highest in $[Co(NH_3)_6][Co(CN)_6]$ and the yield of $^{60}Co(CN)_6^{3-}$ highest in $[Co(NH)_3][Fe(CN)_6]$.

The above-described experiments are related to Müller's experiments (cf. sect. 1.3) where e.g. the $^{185}Re(n,\gamma)^{186}Re$-reaction was studied in mixed crystals of K_2ReBr_6 and K_2SnCl_6 [M28]. The results of one of these experiments are shown in table 2; the $^{186}ReO_4^-$-fraction probably represents ligand-deficient Re-complexes, which are not stable in water.

Table 2

Relative yields of ^{186}Re-labelled complexes in reactor-irradiated crystals of K_2ReBr_6 in K_2SnCl_6 (1:100). From H. Müller [M28]

Complex	Yield (%)
$^{186}ReBr_6^{2-}$	13
$^{186}ReBr_5Cl^{2-}$	7
$^{186}ReBr_4Cl_2^{2-}$	6
$^{186}ReBr_3Cl_3^{2-}$	8
$^{186}ReBr_2Cl_4^{2-}$	11
$^{186}ReBrCl_5^{2-}$	13
$^{186}ReCl_6^{2-}$	32
$^{186}ReO_4^-$	10

From this and similar distributions Müller calculates the dilution of the original six Br-ligands and assumes that this represents the zone of the crystal that is affected (cf. e.g. M27); if one takes it that this zone is spherical, the figures in table 2 yield a radius of about 5.5 Å. This is assumed to represent the range of the recoil atoms and since the distance between central atoms in crystals of this type is about 7 Å, replacement collisions between central atoms should then be excluded.

The calculation of the size of this reaction zone is based on the assumption that the six original ligands are diluted with all other ligands

present within the zone. How the ligands are liberated from the central atoms is not discussed. If not all ligands are liberated, the zone - and consequently the recoil range - must be larger; therefore Müller's experimental results are not in contradiction with ours - especially since the recoil energy of the heavier ^{186}Re is considerably lower than that of ^{59}Fe (cf. sect. 1.3).

In returning to our own results (fig. 13), we note that the annealing behaviour is the same for ^{59}Fe originating from a trisdipyridyl and a hexacyanide complex, namely a transfer of "free" ^{59}Fe to the $^{59}Fe(dipy)_3^{2+}$ -fraction, and practically no changes in the other fractions. This can be understood in terms of the solid-state exchange mechanism proposed for annealing of recoil-^{60}Co in $Co(dipy)_3(ClO_4)_3$ [K9, N2]; it is assumed that the energy required is supplied by an electron-hole recombination, the electron being released from traps of varying depths, and the hole being associated with the recoiled atoms.

Solid-state exchange has also been experimentally demonstrated by Mössbauer spectroscopy [N4]. In these studies $^{57}Co^{2+}$ was doped into $Co(dipy)_3(ClO_4)_3$ and used as source (cf. sect. 2.4); immediately after the preparation only free ^{57}Fe was detected, but after a few days resonances from iron trisdipyridyl complexes appeared; here it is improbable that release of charge carriers should be important.

A similar annealing pattern was observed by Saito et al. [S1] in their studies with $[Co(NH_3)_6][Co(CN_6]$ and $[Co(NH_3)_6][Fe(CN)_6]$, where ^{60}Co is transferred from the Co^{2+} -fraction to $Co(NH_3)_6^{3+}$ with no changes in the small $^{60}Co(CN)_6^{3-}$-yield. It thus appears that in some systems these solid-state reactions are more probable than recombinations of recoil fragments. This shows the importance of the crystal lattice for the final fate of the recoil atoms, but of course prevents the use of annealing studies to elucidate the nature of the immediate effects of (n, γ)-recoil.

Lazzarini [L1] made annealing studies on reactor-irradiated $cis[Coen_2(NO_2)_2][CoEDTA]\cdot 3H_2O$ and found correlated transfer of activity into the two different complexes. The results were taken as evidence of isotope exchange annealing, since the release of electrons would affect the two annealing reactions in parallel. However, recombinations of recoil fragments could equally well have a common trigger mechanism. In principle the two types of annealing can be distinguished in experiments with specifically enriched samples, but unfortunately this is not possible in practice for cobalt compounds, since cobalt has only one stable isotope, ^{59}Co.

5. REACTIONS IN IRON COMPOUNDS

II. MÖSSBAUER EXPERIMENTS

The iron isotope ^{57}Fe can be produced in various nuclear reactions, and the chemical effects of these reactions can - at least in principle - be studied by Mössbauer emission spectroscopy (cf. sect. 2.4). In our own experiments ^{57}Fe has been generated in two reactions (fig. 14):

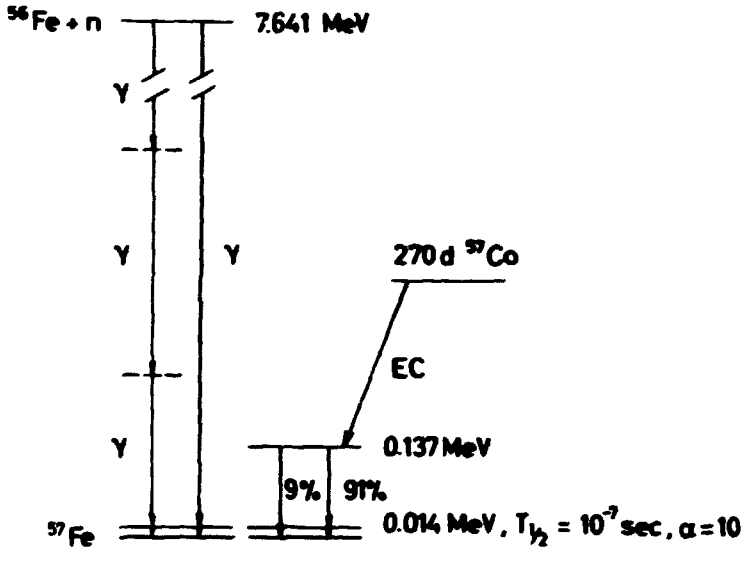


Fig. 14. Formation of the Mössbauer nucleus ^{57}Fe.

Neutron capture in the stable isotope ^{56}Fe (σ_{abs} = 2.7b) gives ^{57}Fe with an excitation energy of 7.641 MeV. The subsequently emitted γ-cascades lead in about 50% of the cases to population of the 14 keV Mössbauer level; with nearly equal probability this happens in a direct transition giving a recoil of 544 eV or in a cascade with lower total recoil [C25, G10]. None of the transitions leading to the 14 keV level are significantly converted; the chemical effects of the $^{56}Fe(n,\gamma)^{57}Fe^{x}$-reaction should therefore be comparable with those of the $^{58}Fe(n,\gamma)^{59}Fe$-reaction (fig. 10), since in both cases the initial cause is a mechanical recoil only.

Orbital electron capture (cf. sect. 1.3) in ^{57}Co ($T_{1/2}$ = 270 d) gives ^{57}Fe with an excitation energy of 0.137 MeV; in 91% of the cases the emission of a 0.123 MeV quantum then leads to ^{57}Fe in the 14 keV level. The EC-process normally releases an Auger cascade, which results in the

emission of up to seven orbital electrons. The probabilities of the charge states of ^{57}Fe following electron capture in $^{57}Co^{o}$, $^{57}Co^{2+}$, and $^{57}Co^{3+}$ were calculated by Pollak [P9] and are presented in table 3. The loss of electrons may have chemical consequences as discussed in sects. 1.3 and 5.1. The subsequent emission of the 0.123 MeV quantum only gives a recoil of about 0.1 eV and can be ignored.

Table 3

Probabilities, in per cent, of charge states of ^{57}Fe formed by $^{57}Co(EC)^{57}Fe$-reactions. After Pollak [P9]

Initial ^{57}Co-state	Resulting ^{57}Fe-state								
	Fe^{o}	Fe^{+}	Fe^{2+}	Fe^{3+}	Fe^{4+}	Fe^{5+}	Fe^{6+}	Fe^{7+}	Fe^{8+}
Co^{o}	1	5	21	25	29	14	4	-	-
Co^{2+}	-	-	5	21.5	25.3	29.5	14.2	4.1	-
Co^{3+}	-	-	-	5	21.5	25.3	29.5	14.2	4.1

5.1. Mössbauer Spectroscopy and Chemical Effects of Nuclear Reactions in Solids

Mössbauer investigations of chemical effects of nuclear reactions have proceeded surprisingly independent of other "hot-atom" studies under the name of "After-effects" (cf. sect. 2.4 and references therein).

The first observation of "after-effects" was made by Wertheim [W5] who found ^{57}Fe nearly equally distributed between Fe^{2+} and Fe^{3+} in sources of ^{57}CoO. This indicated that some of the higher charge states (cf. table 3) had been partly neutralized before the emission of the Mössbauer quantum, and Pollak [P9] calculated a mean lifetime for Fe^{3+} of about $1.4 \cdot 10^{-7}$ s.

However Triftshäuser and Craig [T7] made Mössbauer measurements in delayed coincidence with the preceding 123 keV quantum (cf. fig. 14) in various compounds and showed that no such decay took place in the time interval $4\text{-}200 \cdot 10^{-9}$ s. Therefore the observed $^{57}Fe^{3+}$ cannot be a transient species, but must be stabilized in the lattice. Various mechanisms have been proposed for compounds of different types:

In covalent compounds like oxides, doped with $^{57}Co^{2+}$, it appears that $^{57}Fe^{3+}$ can be stabilized by charge compensation from lattice defects or impurities acting as electron traps (for a discussion cf. e.g. ref. W7).

Ingalls and Depasquali [I1] observed that in ionic compounds crystal water favoured stabilization of higher charge states, and Friedt and Adloff [F23] proposed that the mechanism was a radiolysis of H_2O by the Auger electrons followed by an oxidation of Fe^{2+} by OH-radicals (or alternatively a stabilization of Fe^{3+}):

$$H_2O \rightsquigarrow OH + H$$

$$OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- .$$

In $^{57}CoCl_2 \cdot nH_2O$ the yield of $^{57}Fe^{3+}$ increased with the number of H_2O and with the temperature, suggesting that the oxidation depends upon a migration of the OH-radicals or that the Fe^{2+} is more loosely bound in the lattice than Fe^{3+}. The observation [W6] that γ-irradiation of hydrated ferrous absorbers resulted in formation of Fe^{3+} supported the theory. Analogous effects have been proposed [F26] for compounds containing NH_3, from which NH_2-radicals are formed.

In anhydrous crystals higher charge states may be stabilized by cation vacancies produced by local radiolysis [F25]. For such compounds it has been shown that the probability of stabilization of $^{57}Fe^{3+}$ is correlated with the difference in lattice energy on replacing Fe^{2+} in the matrix by Fe^{3+}, and thus it depends upon the thermodynamic properties of the lattice [C24] (for a discussion of these results cf. e.g. ref. M7).

When ^{57}Co decays in a cobalt(III)-compound, the Mössbauer spectra often indicate the formation of ^{57}Fe(II)-species; these cannot be formed directly by the Auger charging. Hazony and Herber [H19] argued that since iron ions are larger than cobalt ions, they will experience a pressure in a cobalt compound. This can in principle lead to an apparent reduction [C10, C11, H23] caused by a redistribution of electrons, whereby ferric compounds give Mössbauer absorption spectra similar to those of ferrous compounds. This hypothesis does not hold for a series of cobalt(III)-complexes, since the effects persist when the ^{57}Co-labelled complexes are

doped into the analogous Fe(III)-compounds [F11, S5]. In such cases it appears that the Fe(II)-species are formed by radiolysis of the molecular environment [B3, F11, S5]; the mechanism may therefore be related to the "Auger electron reaction mechanism" proposed by Geislar and Willard for isomeric transitions in organic halides (cf. sect. 1.3). A more detailed discussion of a specific case is presented in sect. 5.3.

In other cases chemical effects of the $^{57}Co(EC)^{57}Fe$-reaction appear to be different from those of radiolysis. Thus in $^{57}Co(III)(1.10\ phenanthroline)_3\ (ClO_4)_3 \cdot 2H_2O$ some $^{57}Fe^{2+}$ has been observed (cf. sect. 5.4 and ref. J1). This is taken as evidence of Coulomb fragmentation (cf. sect. 1.3). Pollak's calculation (table 3) shows that a significant proportion of the ^{57}Fe is formed with a charge 5 units higher than that of the parent ^{57}Co; this should according to computer simulations (cf. sect. 1.4) provide sufficient Coulomb energy to give an atomic displacement provided that the charged ion has a sufficiently long lifetime. Consistent with this, the $^{57}Co(EC)^{57}Fe$-reaction does not have observable chemical effects in large molecules with conjugated ring systems (e.g. vitamin B_{12}), where a rapid electron transport can give charge recovery before fragmentation [N3]. Our results obtained for $^{57}Co(CN)_6^{3-}$ (sect. 5.5) are interpreted along the same lines.

In a different type of experiments Mössbauer levels are populated via induced nuclear reactions (cf. sect. 2.4), but generally the applied targets have been of little interest from a hot-atom chemistry point of view. In a single experiment Berger [B14] irradiated $FeSO_4 \cdot 7H_2O$ in a thermal neutron beam and measured simultaneously the Mössbauer spectrum of the ^{57}Fe formed by the $^{56}Fe(n,\gamma)^{57}Fe$-reaction (fig. 14). He found that about 40% of the detected ^{57}Fe comes to rest in the lattice as Fe^{3+}. This result cannot be interpreted in terms of the radiolysis model since no converted transitions - and consequently no Auger cascades - have been observed in the decay of excited ^{57}Fe. In radiochemical experiments with the same compound (cf. sect. 4.1) we found only 2% $^{59}Fe^{3+}$.

A Mössbauer beam experiment is described in more detail in sect. 5.2.

In most hot-atom studies based on Mössbauer spectroscopy no attention has been paid to the possibility that the f-factors (cf. sect. 2.4) for the different species at a given temperature may not be the same. If the interpretation of the results is only qualitative, this may be of minor importance, but the problem must be considered when results obtained with Mössbauer spectroscopy and radiochemical analysis are compared (cf. sect. 5.2) or when

different systems are investigated in parallel (cf. sect. 5.5).

The first pertinent observation was made already in 1964 by Stone and Pillinger [S30]. They investigated the emission spectrum of ^{237}Np in NpO_2 and found a much lower intensity when the ^{237}Np was formed by α-decay of ^{241}Am than when it was formed by β-decay of ^{237}U. The α-emission gives the ^{237}Np-atom a recoil energy of 93 keV, but it is estimated [K1] that it will be slowed down completely within $4 \cdot 10^{-13}$ s. Since the lifetime of the Mössbauer level is much longer ($6.3 \cdot 10^{-8}$ s), it appears that some ^{237}Np-atoms end in positions in the lattice where the Debye temperature is lower than in the rest of the lattice.

Mössbauer experiments based on induced nuclear reactions (beam experiments) indicate that in monoatomic solids, the f-factor is not greatly reduced, even after violent nuclear events. Thus in metallic iron both the $^{56}Fe(n,\gamma)^{57}Fe$-reaction [B15] and the $^{56}Fe(d,p)^{57}Fe$-reaction [G5] give ^{57}Fe with an emission spectrum that is not significantly different from absorber spectra; therefore the ^{57}Fe must end up in regular lattice sites. An accurate determination [C12] of the magnetic splitting in the spectrum of ^{57}Fe resulting from $^{56}Fe(n,p)^{57}Fe$ could even demonstrate that the temperature of the lattice around the ^{57}Fe had fallen to ambient before the emission of the 14 keV quantum. These findings are in agreement with the results of computer simulations (cf. sect. 1.4).

The experimental results on reactions with a substantial recoil in more complicated structures are less consistent, but on the whole show that the f-factors are lower than for reactions in monoatomic solids. Christiansen et al. [C12] found that the f-factor of ^{57}Fe formed by $^{56}Fe(d,p)^{57}Fe$-reactions in Fe_2O_3 was - at room temperature - about 90% of the value in metallic iron. Larger differences were observed in spectra of ^{57}Fe which was either Coulomb excited in the source [R3] or recoil implanted [S26, S27]. In Gd_2O_3 the $^{155}Gd(n,\gamma)^{156}Gd$ and $^{157}Gd(n,\gamma)^{158}Gd$-reactions result in Mössbauer spectra consistent with an f-factor of only about 60% of that in metallic gadolinium [F19]. Hafemeister and Shera [H3] measured the Mössbauer spectra of ^{40}K formed by the $^{39}K(n,\gamma)^{40}K$-reaction in K, KCl, and KF and estimated on the basis of partly experimentally determined f-factors that (op. cit.) "the recoilless emission process is not greatly impaired by the method of formation of the source". Later, however, Ray and Puri [R2] calculated an f-factor on the basis of a theoretical phonon frequency distribution for potassium and argued that the experimentally determined values were a factor of 2 to 3 too low.

As the above discussion indicates, a reduced f-factor in e.g. an oxide after a violent nuclear event is normally taken as evidence that the Mössbauer nuclei do not all reach a normal lattice position. It has, however, also been argued [D4, H17, M25] that a reduction of f-factors could result from a local heating of the lattice as a result of the nuclear event; such an effect would depend upon the rate of heat diffusion and should therefore be more pronounced for non-metals. In the case of $^{56}Fe(n,\gamma)^{57}Fe$-reactions (cf. sect. 5.2) these effects can hardly be invoked, since the lifetime of the Mössbauer level is so long (10^{-7} s) that the modest recoil energy (max. 544 eV) must be dissipated long before the 14 keV quantum is emitted.

If the nuclear reaction does not give a substantial mechanical recoil, the formed Mössbauer nucleus may remain in its lattice site (cf. sect. 5.4), but the immediate surroundings can be modified. The possible changes in f-factors may be estimated from various absorber measurements. Thus two regular, but different, lattice sites in soluble Prussian blue and in an iron double complex (cf. sects. 4.2 and 4.3 and references therein) have f-factors which differ only about 10% at room temperature. The same was found to be the case for some iron-containing minerals [e.g. B8]. Atoms which have had bonds to ligands broken (cf. sects. 5.3-5.5) may be in a situation similar to that of atoms in or near the surface of a solid. This situation has been treated theoretically by i.a. Maradudin and Melngailis [M10], and on the basis of such calculations we estimate roughly that the loss of one of six ligands could result in a reduction of the f-factor of up to 50% at room temperature (cf. sect. 5.5).

The possibility of heated localized modes following the $^{57}Co(EC)^{57}Fe$-reaction was considered by Hoy and Wintersteiner [H25], who observed a time-dependent recoilless fraction at a Fe^{3+}-site formed in $CoSO_4 \cdot 7H_2O$; however, the effect could not be seen in other similar matrices.

As appears from the formula for f-factors given in sect. 2.4, they depend - ceteris paribus - exponentially upon the lattice temperature. Therefore it is in principle possible to determine absolute values of f-factors, by recording Mössbauer spectra of a specific source or absorber at various temperatures [K8]. However, in the case of sources it must be taken into consideration that the chemical effects of the nuclear reaction may be temperature-dependent, which will in itself change the resonance intensities. An investigation of this type is discussed in sect. 5.5.

5.2. The $^{56}Fe(n,\gamma)^{57}Fe$-Reaction in Ferrous Oxalate and Potassium Ferrocyanide. A Beam Experiment

In order to investigate the possibilities of using Mössbauer spectroscopy in the study of chemical effects of $^{56}Fe(n,\gamma)^{57}Fe$-reactions, we made neutron beam experiments of the type described by i.a. Berger [B14] (cf. sects. 2.4, 5.0, and 5.1). As targets were used the two compounds $K_4Fe(CN)_6 \cdot 3H_2O$ and $FeC_2O_4 \cdot 2H_2O$, in which we previously (cf. sects. 4.2 and 4.1) investigated the chemical fate of recoil-^{59}Fe. The experimental techniques are described in detail in ref. F15, and in references therein, and the "set-up" is shown in fig. 15.

Fig. 15. The Mössbauer beam experiment at the Danish reactor DR 3. A thermal neutron beam is taken out through an evacuated and heavily shielded flight tube. About 1.5 m from the reactor face the beam hits a target which forms an angle of 45° with the tube axis. The Mössbauer "set-up" proper, in which the target serves as source, has a vertical axis.

As may be inferred from fig. 15 and its caption, the greatest problem in such experiments is a high background radiation which mainly arises from thermal neutrons that are captured or scattered in the target and the target holder. Therefore the "signal to noise" ratio is much lower than in more conventional Mössbauer experiments.

In order to ensure that a curvature of the base line in the recorded spectra was not mistaken for a weak, broad resonance, two different detectors were used: (1) A commercial proportional counter, which shows a reduction in count rate at resonance (cf. sect. 2.4), and (2) a special resonance counter [F9] constructed after the same principle as described by e.g. Mitrofanov [M20]. This counter detects the excitations of nuclei that have captured a Mössbauer quantum; it therefore shows an increase in count rate at resonance.

No resonances could be detected with a target of $K_4Fe(CN)_6 \cdot 3H_2O$, but small resonances with the right signs for the two detectors were obtained with $FeC_2O_4 \cdot 2H_2O$; they show that some recoil-^{57}Fe is stabilized as Fe^{2+}. We made no attempt to determine the absolute value of the f-factor of recoil-^{57}Fe in $FeC_2O_4 \cdot 2H_2O$. Instead the total spectral intensity was compared with that obtained with the target replaced by a source of ^{57}Co-doped $FeC_2O_4 \cdot 2H_2O$ (cf. sect. 5.3). This comparison showed that the probability of detection of ^{57}Fe formed by an $^{56}Fe(n, \gamma)^{57}Fe$-reaction is only about half of that of detection of ^{57}Fe formed by a $^{57}Co(EC)^{57}Fe$-reaction. An even greater difference must be assumed for reactions in $K_4Fe(CN)_6 \cdot 3H_2O$.

As pointed out in sect. 5.1 it is not reasonable to assume that the reduction in f-factor is due to a local heating of the lattice. If we therefore assume (cf. sect. 5.0) that the two reactions $^{56}Fe(n, \gamma)^{57}Fe$ and $^{58}Fe(n, \gamma)^{59}Fe$ have the same chemical effects, we must conclude that the $^{59}Fe(II)$ found in radiochemical analysis of neutron-irradiated $FeC_2O_4 \cdot 2H_2O$ (cf. sect. 4.1) does not sit in regular lattice positions. For (n, γ)-reactions in $K_4Fe(CN)_6 \cdot 3H_2O$ the radiochemical experiments (cf. sect. 4.2) suggested that most of the ^{59}Fe is in the form of Fe^{2+} or Fe^{3+}, but in the Mössbauer experiment we did not detect the resonances corresponding to $^{57}Fe^{2+}$ and $^{57}Fe^{3+}$. Probably the f-factor of "free" ^{57}Fe in a $K_4Fe(CN)_6 \cdot 3H_2O$-lattice is low, but it can also be imagined that the ^{57}Fe is situated in various surroundings and that the individual, different resonances are too weak to be detected.

These findings are in agreement with the results of other measurements of the Mössbauer effect after violent nuclear events (cf. sect. 5.1). It therefore appears that an application of Mössbauer spectroscopy in the study of chemical effects of (n, γ)-reactions in complex solids requires a determination of the individual f-factors for the possible recoil products. Various improvements of our experimental set-up are possible [F15]; however, considering the difficulties in obtaining reasonably accurate results in source experiments (cf. sect. 5.5), it appears that further beam experiments are not worth-while with the present-day techniques.

5.3. The $^{57}Co(EC)^{57}Fe$-Reaction in Ferrous Sulphate and Iron Oxalates

In order to compare the chemical effects of $^{57}Co(EC)^{57}Fe$-reactions with those of $^{58}Fe(n,\gamma)^{59}Fe$-reactions (cf. sect. 4.1) we doped $FeSO_4 \cdot 7H_2O$, $FeC_2O_4 \cdot 2H_2O$, $Fe_2(C_2O_4)_3 \cdot xH_2O$, and $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ with ^{57}Co and measured them as Mössbauer sources. The results were further compared with radiolytic data found in the literature; some of these were obtained by Mössbauer measurements of irradiated absorbers.

Source spectra of $Fe(^{57}Co)SO_4 \cdot 7H_2O$ [F8] were recorded at room temperature and contained a quadrupole doublet (Δ = 3.1 mm/s) corresponding to $^{57}Fe^{2+}$ and unresolved resonances corresponding to $^{57}Fe^{3+}$. The relative intensities were 63 $\pm$ 4% and 37 $\pm$ 4% respectively; this distribution is the same as observed after $^{56}Fe(n,\gamma)^{57}Fe$-reactions [B14]. The spectra were also similar to those recorded [G11] for γ-irradiated $FeSO_4 \cdot 7H_2O$-absorbers. We originally [F8] took this as evidence that the role of the nuclear reaction in a hot-atom event was only to supply energy to the lattice and that the product yields were determined by the lattice properties. The discrepancy with the radiochemical results for $^{58}Fe(n,\gamma)^{59}Fe$-reactions where only 2% ^{59}Fe(III) were found, was explained as a result of a rapid annealing of the recoil species.

Source spectra of $Fe(^{57}Co)C_2O_4 \cdot 2H_2O$ [F8, F9] were recorded at room temperature and apparently contain two resonance lines corresponding to an $^{57}Fe^{2+}$-doublet (Δ = 1.75 mm/s). One of the lines, however, was slightly stronger than the other and was found to hide an unresolved $^{57}Fe^{3+}$-resonance. The relative intensities of the $^{57}Fe^{2+}$ and $^{57}Fe^{3+}$-resonances were 89.8 $\pm$ 0.4% and 10.2 $\pm$ 0.4% respectively. Later the measurements were repeated at -125°C with the same results. If the sources were dehydrated, the $^{57}Fe^{3+}$-intensity only dropped to about 8%; this indicates that stabilization of $^{57}Fe^{3+}$ by radiolysis of H_2O (cf. sect. 5.1) does not play an important role. The relative resonance intensity of $^{57}Fe^{3+}$ from $^{57}Co(EC)^{57}Fe$-reactions is the same as the yield of $^{59}Fe^{3+}$ from $^{58}Fe(n,\gamma)^{59}Fe$-reactions (cf. sect. 4.1). This agrees with the hypothesis of similar effects of the two reactions, but our Mössbauer beam experiment (cf. sect. 5.2) demonstrated that this is not sufficient evidence.

Absorber spectra of γ-irradiated (1400 Mrads) $FeC_2O_4 \cdot 2H_2O$ did not indicate any radiation damage [G11]; also other investigations [e.g. S35] have shown that ferrous oxalate is extremely stable against γ-radiolysis, although a slight formation of CO_2 (G = 0.53) has been observed [D10].

How Fe^{3+} is stabilized in $FeC_2O_4 \cdot 2H_2O$ is still unsettled, but there is little reason to believe that the mechanism is the same for products of various nuclear reactions. No direct relation with radiolysis effects could be established, but it is worth noting that the yield of $^{57}Fe^{3+}$ is low and the radiolytic stability of $FeC_2O_4 \cdot 2H_2O$ is high.

Freshly prepared sources of $Fe_2(^{57}Co)(C_2O_4)_3 \cdot xH_2O$ [S20] show spectra nearly identical with the spectra obtained with ferrous oxalate - only the relative yields were slightly different: 80% Fe^{2+} and 20% Fe^{3+}. A similar reduction of iron was apparent in absorber spectra of γ-irradiated (200 Mrads) $Fe_2(C_2O_4)_3 \cdot xH_2O$, which showed a substantial formation of ferrous oxalate [S2]. In another study [S35] the G-value for reduction was found to be about 10.

On the other hand, the chemical effects of $^{58}Fe(n,\gamma)^{59}Fe$-reactions in $Fe_2(C_2O_4)_3 \cdot xH_2O$ were shown (cf. sect. 4.1) to be completely different with formation of only a few per cent $^{59}Fe(III)$.

$K_3Fe(C_2O_4)_3 \cdot 3H_2O$ and similar compounds have been investigated more closely than the compounds treated above, and a more detailed discussion of the results is possible.

Source spectra of $K_3Fe(^{57}Co)(C_2O_4)_3 \cdot 3H_2O$ (fig. 16) [F11] were recorded at room temperature and contained a single broad line corresponding to the $Fe(C_2O_4)_3^{3-}$-complex and a doublet with a splitting of 2.32 mm/s; the relative intensities of the resonances were 31 ± 5% and 69 ± 5% respectively. In a dehydrated source the values were nearly the same - 25 and 75% respectively. Further a source was prepared from pure $K_3Co(C_2O_4)_3 \cdot 3H_2O$; the relative intensity of the doublet was now only 57% (this lower value is discussed later), but the parameters were, within the accuracy of the measurements, the same as in $K_3Fe(C_2O_4)_3 \cdot 3H_2O$. A similar doublet has been observed by Friedt and Asch [F24] with the cobalt complex. Since the same ^{57}Fe-species is formed in the iron and the cobalt compound, neither pressure effects (cf. sect. 5.1) nor faulty doping can be invoked to explain the results.

The parameters of the source doublet correspond closely to those of a doublet observed by Bancroft et al. [B9] with irradiated absorbers of $K_3Fe(C_2O_4) \cdot 3H_2O$ and ascribed to $Fe(C_2O_4)_2^{2-}$. Furthermore, evidence of the existence of the $C_2O_4^-$-radical has been obtained i.a. in solid-state photolysis of the $Fe(C_2O_4)^{3-}$-ion [S6]. This suggests the following overall reaction:

$$Fe(C_2O_4)_3^{3-} \rightsquigarrow Fe(C_2O_4)_2^{2-} + C_2O_4^{-} ,$$

which may thus account both for γ-radiolysis and chemical effects of the $^{57}Co(EC)^{57}Fe$-reaction. Water does not participate in the proposed process in agreement with the observation that the effects are essentially the same in hydrated and anhydrous potassium trisoxalatoferrate.

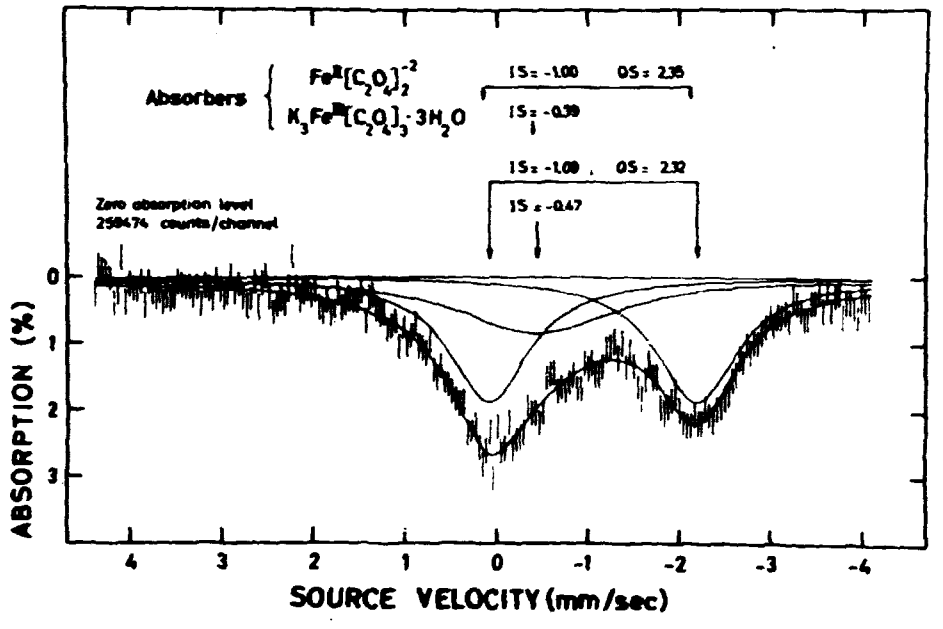


Fig. 16. Mössbauer source spectrum of potassium trisoxalatoferrate [F11]. Parameters for the $Fe^{II}[C_2O_4]_2^{2-}$-ion are taken from ref. B9.

In a similar study of the γ-radiolysis of $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ Temperley and Pumplin [T3] attempted to prepare $K_2Fe(C_2O_4)_2 \cdot 2H_2O$ for identification. They were not able to obtain a pure well-defined product, but absorber measurements showed two doublets which at room temperature had the quadrupole splittings 2.58 and 3.90 mm s^{-1}. They were ascribed to cis- and trans-$K_2Fe(C_2O_4)_2 \cdot (H_2O)_2$. The splitting for the cis-form is reasonably close to the splitting of the new ^{57}Fe-species formed in our $K_3Fe(C_2O_4)_3 \cdot 3H_2O$-source experiment; a cis-form is also what one would expect to result from the loss of a $C_2O_4^{-}$-radical from an octahedrally coordinated chelate iron complex.

Sugimori [S35] has proposed that in radiolysis of trisoxalatoferrate the whole complex molecule is excited, and an electron is then transferred from one of the ligands to the central metal cation:

$$[Fe^{III}(C_2O_4)_3]^{3-} \xrightarrow{\gamma} Fe^{III}(C_2O_4)_3^{3-\,*}$$

$$\rightarrow \left[\begin{array}{c} O \quad O \\ \diagdown\!\!\diagup \\ C \quad\quad Fe^{II}(C_2O_4)_2 \\ | \\ C \\ \diagup\!\!\diagdown \\ O \quad O \end{array}\right]^{3-} \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + C_2O_4^-$$

The $C_2O_4^-$-radical eventually attacks a $[Fe^{III}(C_2O_4)_3]^{3-}$-ion to form CO_2 and $[Fe^{II}(C_2O_4)_3]^{4-}$.

Returning to our source experiments we note that the intensity of the doublet attributed to $^{57}Fe^{II}(C_2O_4)_3^{2-}$ was slightly higher in the $K_3Fe(C_2O_4)_3 \cdot 3H_2O$-matrix than in the $K_3Co(C_2O_4)_3 \cdot 3H_2O$; on the other hand it has been shown [S35] that $K_3Co(C_2O_4)_3 \cdot 3H_2O$ is more sensitive to γ-radiolysis than $K_3Fe(C_2O_4)_3 \cdot 3H_2O$. This may be understood as an effect of the energy migration demonstrated by Dharmawardena and Maddock [D8]; they incorporated $Fe(C_2O_4)_3^{3-}$ in the isomorphic, but radiation-resistent $K_3Al(C_2O_4)_3 \cdot 3H_2O$ and found that on γ-irradiation the absorbed radiolytic energy migrates into the iron complex and causes dissociation. In our source experiments dissociation of a newly formed $^{57}Fe(C_2O_4)_3^{3-}$-complex may be prevented if some excitation energy is transferred to neighbouring complexes; this effect should be more pronounced in the less radiation-resistent $K_3Co(C_2O_4)_3 \cdot 3H_2O$. A closer investigation of this possible mechanism requires determination of f-factors as discussed in sect. 5.5.

As already pointed out in sect. 4.1 the relative resonance intensity of $^{57}Fe(II)$ formed by $^{57}Co(EC)^{57}Fe$-reactions and the yield of $^{59}Fe(II)$ formed by $^{58}Fe(n,\gamma)^{59}Fe$-reactions in $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ are similar; however, if the $^{57}Fe(II)$-species is indeed $^{57}Fe(C_2O_4)_2^{2-}$, its thermal stability must be much higher than that of the $^{59}Fe(II)$. Therefore the two nuclear reactions cannot have the same chemical effects.

5.4. The $^{57}Co(EC)^{57}Fe$-Reaction in Soluble Prussian Blue and in a Cobalt "Double Complex"

In further comparative studies analogues to the special compounds described in sects. 4.2 and 4.3 were used as Mössbauer sources [F12, S23]. These investigations were undertaken mainly to establish whether the $^{57}Co(EC)^{57}Fe$ can lead to a displacement of the ^{57}Fe from the ^{57}Co-site.

Sources of soluble Prussian blue, $KFe^{III}[Fe^{II}(CN)_6] \cdot H_2O$ (cf. sect. 4.2), were precipitated with $Fe^{III}(CN)_6^{3-}$ from a solution containing Fe^{2+} and carrier-free $^{57}Co^{2+}$ [F12]. Hereby $^{57}Co^{2+}$ is incorporated in a Fe^{3+}-site, charge balance being obtained with a nearby $Fe^{III}(CN)_6^{3-}$ complex ion in a $Fe^{II}(CN)_6^{4-}$-site. The emission spectra (fig.17) were recorded at room temperature and exhibit a strong doublet corresponding to $^{57}Fe^{3+}$ and a weak doublet corresponding to $^{57}Fe^{2+}$. The relative intensity of the $^{57}Fe^{2+}$-doublet

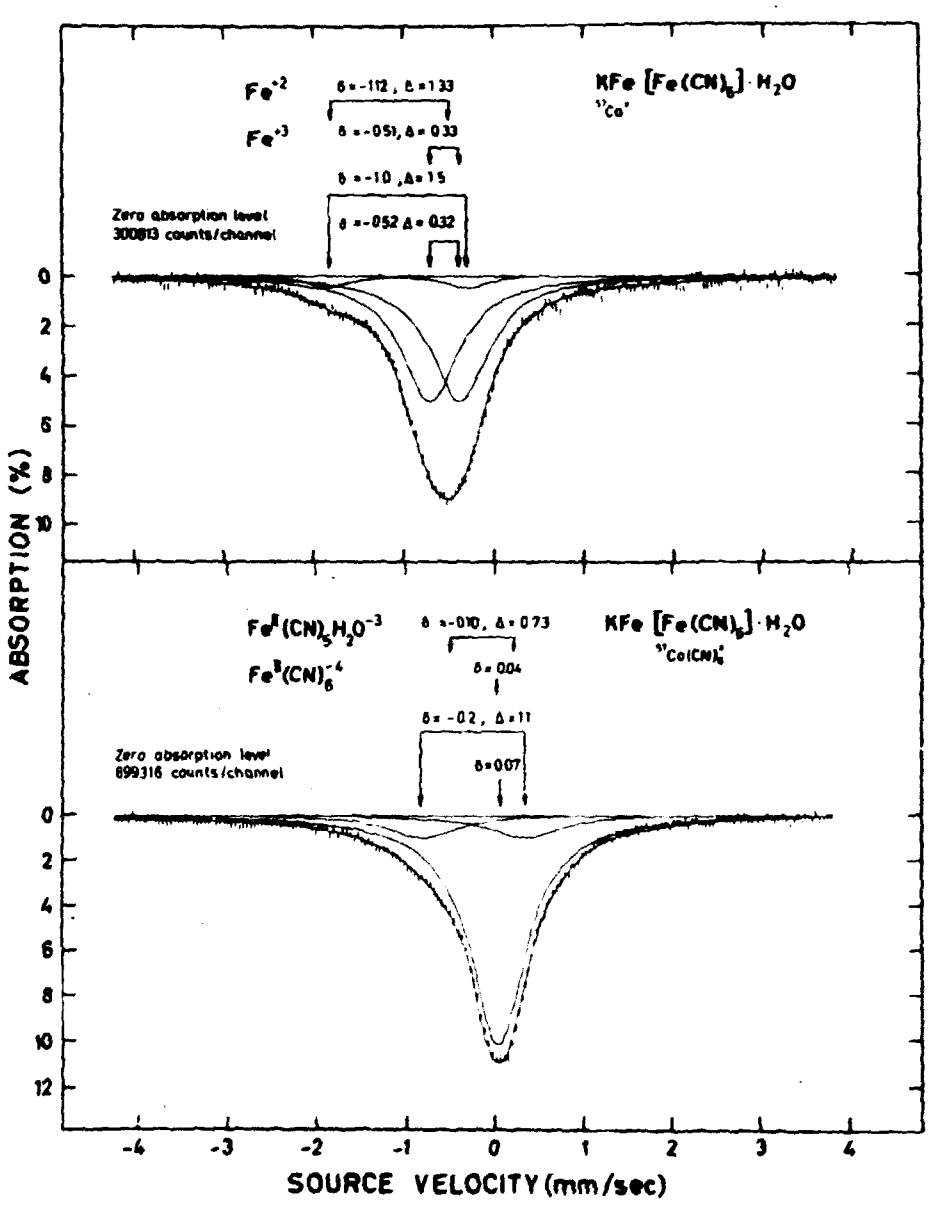


Fig. 17. Mössbauer source spectra of soluble Prussian blue doped with ^{57}Co as indicated [F12].

was found to vary with details in the preparation [F12] and was, in the presumably purest source, practically zero. Therefore the EC-process cannot transfer the nascent ^{57}Fe from an ionic to a complex site.

$KFe[Fe(CN)_6]\cdot H_2O$ was further doped with $^{57}Co(CN)_6^{3-}$, which occupies a $Fe^{II}(CN)_6^{4-}$-site, with a nearby Fe^{2+}-ion in an Fe^{3+}-site. This doping is a crucial point in the experiments described here and in sect. 5.5. Cobalt is readily complexed by cyanide to form a pentacyanide [H31], but the addition of the sixth CN-ligand is slow and probably dependent on autocatalysis [S16]. Therefore the preparation of carrier-free $^{57}Co(CN)_6^{3-}$ [F12] was checked carefully by electrophoresis (cf. sect. 2.2 and ref. R1). The source material was then prepared by precipitating $KFe[Fe(CN)_6]\cdot H_2O$ from a solution containing $^{57}Co(CN)_6^{3-}$. After the recording of the spectra, the sources were again brought into colloidal solution and analysed once more. We found these checks to be especially important when it became apparent that the result of the $^{57}Co(EC)^{57}Fe$-reaction was formation of a pentacyanide (see below).

The emission spectra (fig. 17) of $^{57}Co(CN)_6^{3-}$ doped sources exhibit a strong single resonance corresponding to $^{57}Fe(CN)_6^{4-}$. A small asymmetry indicates the presence of unresolved resonances, and various computer fits suggest a doublet ($\Delta = 1.1$ mm/s; relative intensity 25%) that could be ascribed to a ferrous pentacyanide. Alternatively the asymmetry could be accounted for by assuming a single line, which might arise from $^{57}Fe^{3+}$ with a large isomer shift. Since, however [S23], the spectrum of $K_4[Fe(^{57}Co)(CN)_6]\cdot 3H_2O$ was found to contain a doublet with the same parameters as in the Prussian blue, but a yield of 82%, we conclude that ferrous pentacyanide was actually observed in the Prussian blue source.

These experiments do not indicate any displacement of the ^{57}Fe formed by the $^{57}Co(EC)^{57}Fe$-reaction; this result is completely different from the result of the radiochemical experiments with the $^{58}Fe(n,\gamma)^{59}Fe$-reaction, which was found to displace the ^{59}Fe in nearly all the cases.

Cobalt(III)trisdipyridyl and cobalticyanide form a crystalline precipitate which was analysed [S23] and found to be $[Co(dipy)_3][Co(CN)_6]\cdot 2H_2O$. This compound has to our knowledge not been described before. Sources were prepared with each of the two complexes specifically labelled with ^{57}Co, and in addition various sources containing only one of the complexes were prepared. The emission spectra of these sources were all measured both at room temperature and -125°C, but only the small expected temperature shifts [K8] were observed.

The spectra of $K_3{}^{57}Co(CN)_6$ and $K_3Fe(^{57}Co)(CN)_6$ were resolved in a doublet which was ascribed to a ferripentacyanide, and a doublet corresponding to the parent hexacyanide. In the spectra of $[^{57}Co(dipy)_3](ClO_4)_3$ and $[Fe(^{57}Co)(dipy)_3](ClO_4)_3$ doublets were observed, corresponding to $^{57}Fe(dipy)_3^{3+}$, $^{57}Fe(dipy)_3^{2+}$, and $^{57}Fe^{2+}$. In analogy with the Prussian blue case, the spectra of $[^{57}Co(dipy)_3]\,[Co(CN)_6]\cdot 2H_2O$ and $[Co(dipy)_3]\,[^{57}Co(CN)_6]\cdot 2H_2O$ were completely different, but each of them was similar to the spectrum of the individual complex. The relative intensities of the resonances in the spectra of the four most important sources are shown in table 4.

Table 4

Relative intensities of resonances in Mössbauer sources measured at -125°C [S23]

Source	^{57}Fe-species	Intensity: %
$K_3{}^{57}Co^{III}(CN)_6$	$Fe^{III}(CN)_6^{3-}$ "$Fe^{III}(CN)_5$"	20 ± 3 80 ± 3
$[Co^{III}(dipy)_3][^{57}Co^{III}(CN)_6]\cdot 2H_2O$	$Fe^{III}(CN)_6^{3-}$ "$Fe^{III}(CN)_5$"	28 ± 4 72 ± 4
$[^{57}Co^{III}(dipy)_3](ClO_4)_3$	$Fe^{III}(dipy)_3^{3+}$ $Fe^{II}(dipy)_3^{2+}$ Fe^{2+}	60 ± 4 30 ± 4 10 ± 4
$[^{57}Co^{III}(dipy)_3][Co^{III}(CN)_6]\cdot 2H_2O$	$Fe^{III}(dipy)_3^{3+}$ $Fe^{II}(dipy)_3^{2+}$	76 ± 3 24 ± 3

From the table it appears that neither in the case of the cobalt double complex could an isotope exchange between two different lattice sites be induced by the $^{57}Co(EC)^{57}Fe$-reaction.

Both for the trisdipyridyl complexes and the hexacyanide complexes some similarities were observed between the chemical effects of $^{57}Co(EC)^{57}Fe$-decay and external irradiation.

Thus the formation $Fe^{II}(dipy)_3^{2+}$ in $[Fe^{III}(dipy)_3](ClO_4)_3$ has also been observed [B3] in electron-irradiated absorbers, and a mechanism of the following type was proposed:

$$Fe^{III}RH \rightsquigarrow Fe^{III}R + H$$

$$Fe^{III}RH + H \rightleftharpoons Fe^{II}RH + H^+ .$$

No evidence of ionic iron species was found, neither by Mössbauer nor by ESR spectroscopy; therefore degradation reactions as e. g.:

$$Fe^{III}R \rightarrow Fe^{III} + \dot{R}$$

were considered unlikely [B3]. On the other hand, the spectra of our cobalt and iron trisdipyridyl perchlorate sources indicated formation of some $^{57}Fe^{2+}$ (cf. table 4) although significantly less than previously claimed [M12]. Possibly it is formed by a "Coulomb explosion" (cf. sect. 1.3) of a highly charged ^{57}Fe-trisdipyridyl complex.

The formation of pentacyano, monoaquo-complexes has been observed in radiolysis and photolysis of iron and cobalt hexacyanides in solution [H6, M21, O2, P11, W20] as well as in the solid state [M17]. The mechanisms are still debated, but at least in $Co(CN)_6^{3-}$ it appears [W20] that the photoaquation proceeds as an interchange of an inner sphere CN^--ligand and a water molecule in the outer sphere of the photoexcited $Co(CN)_6^{3-}$. An intermediate $Co(CN)_5^{2-}$ is apparently not formed. Also in the radiolysis of solid ferricyanides water must play an important role, since anhydrous crystals were found to be much more stable than hydrated ones [D3, B4]. Since, however, ^{57}Fe-labelled pentacyanide is readily formed as a consequence of $^{57}Co(EC)^{57}Fe$-reactions in e. g. anhydrous $K_3{}^{57}Co(CN)_6$, the above mechanisms cannot be invoked.

ESR-spectra (cf. sect. 2.5) of electron-X- and Y-irradiated $K_3Co(CN)_6$ [L6, S36, T8] give some evidence of formation of $Co(CN)_5^{3-}$. Possibly the loss of a CN-ligand proceeds via formation of a "di-isocyanide", which is stable only at about liquid-nitrogen temperature [D2]:

$$Co^{III}(CN)_6^{3-} + e^- \rightarrow Co^{II}(CN)_6^{4-} \rightarrow Co^{II}(CN)_4(NC)_2^{4-} \rightarrow Co^{II}(CN)_5^{3-} + CN^- .$$

Similar isocyanides have been proposed as radiolytic products in $K_3Rh(CN)_6$ [M31] and $K_4Ru(CN)_6 \cdot 3H_2O$ [E1]. ESR-studies of irradiated iron-hexa-

cyanides have to our knowledge only been made in alkali-metal halide matrices [R5, S37], but also here evidence was found of formation of isocyanides. "The stability of isocyanide bonds seems to be mainly related to the influence of the lattice since it has been impossible to obtain them in solution and they are unstable in the pure compound" [C4].

Since the ligand field strength of the nitrogen and of cyanide is very low [S18], the Mössbauer spectra of an $Fe(CN)_5(NC)^{3-}$ species may not be different from that of $Fe(CN)_5H_2O^{2-}$ or $Fe(CN)_5^{2-}$ [D3]; we can therefore not, a priori, exclude that the "pentacyanide" resonances which appear in the emission spectra of $^{57}Co(CN)_6^{3-}$ are due to $Fe(CN)_5(NC)^{3-}$. On the other hand, the ^{14}N-hyper-fine coupling observed in the ESR-spectra of the alleged isocyanides is much lower than in similar complexes, and it has been argued [e.g. S36] that the CN-ligands are not rotated fully 180°, but only twisted 10-40°. For a further discussion cf. sect. 5.5.

5.5. Further studies of the $^{57}Co(EC)^{57}Fe$-Reaction in $^{57}Co(CN)_6^{3-}$

The source experiments described in the two previous sections (5.3 and 5.4) only yielded qualitative results. However, the $^{57}Co(CN)_6^{3-}$-complex was found to be well suited for experiments with a more "quantitative" approach [F16, F18].

The seven divalent metal ions, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} precipitate readily with $Co(CN)_6^{3-}$ (as $K_3Co(CN)_6$) and form isomorphic crystals which have a structure similar to that of Prussian blue (fig. 11). The unit cell is cubic (a = 10 - 10.6 Å) with divalent cations and $Co(CN)_6^{3-}$-complexes arranged in a NaCl-structure; charge balance is obtained with cations inside some of the octants. The composition is generally believed to be $Me_3[Co(CN)_6]_2 \cdot xH_2O$, but for nickel also a slightly different form, $Ni_2K_2[Co(CN)_6]_2 \cdot xH_2O$, has been reported; the main lattice is the same, only the charge balance is obtained with K^+-ions. Various amounts of H_2O in the lattices - up to x = 12 - have been reported and it seems to be very loosely bound. (For original literature about the crystal structures cf. ref. F16).

These salts of the $Co(CN)_6^{3-}$-acid are further isomorphic with the corresponding salts of various other hexacyanides i.a. $Fe(CN)_6^{3-}$; it is therefore possible to investigate the influence of both the cation and the anion on the $^{57}Co(EC)^{57}Fe$-event. However, a few preliminary experiments showed that the influence of the complex anion is small. Most important is the observation that the spectral intensity (cf. fig. 19) is the same; therefore

the f-factors are not measurably influenced. In the following only experiments with cobaltihexacyanides are discussed.

Seven different Mössbauer sources were prepared by precipitating $^{57}Co(CN)_6^{3-}$ with the appropriate (see above) cations; after purification the precipitates were dried at room temperature in vacuum. The stoichiometry was checked on inactive material by a modified version of "Job's Method" [F14] and found to agree with literature; for the nickel salt the mixed-cation form was found. Thermogravimetry indicated $x \approx 12$.

Emission spectra of the sources were recorded at ~125°C. All the spectra (with the exception of the spectrum of $Fe_2[^{57}Co(CN)_6]_3$) were resolved in two doublets, one with a quadrupole splitting of 0.5-0.8 mm·s^{-1} and the other with a splitting of 1.6-2.0 mm·s^{-1}. By means of absorber spectra the narrow doublet is readily ascribed to $Fe(CN)_6^{3-}$; the other doublet can be attributed to either $Fe(CN)_5^{2-}$ or possibly $Fe(CN)_5(NC)^{3-}$ (cf. sect. 5.4)

The spectra of $Fe_3[^{57}Co(CN)_6]_2$ were resolved in a single line, ascribed to $Fe(CN)_6^{4-}$, and a doublet with a splitting (~1.2 mm s^{-1}) that is significantly smaller than the splitting of the outer doublets observed with the other sources. The doublet in the $Fe_3[^{57}Co(CN)_6]_2$-spectrum, on the other hand, has parameters similar to those of a doublet observed in the spectra of ^{57}Co-doped $KFe[Fe(CN)_6]$, H_2O and $K_4Fe(CN)_6$, $3H_2O$ (cf. sect. 5.4); we assume that it arises from an Fe(II)-complex. The formation of Fe(II) - and not Fe(III) - complexes in $Fe_3[Co(CN)_6]_2$ is not surprising, since it is well known (cf. sect. 4.2) that a redox reaction,

$$Fe^{III}(CN)_6^{3-} + Fe^{2+} \rightarrow Fe^{II}(CN)_6^{4-} + Fe^{3+},$$

takes place when Prussian blue is prepared from ferricyanide and ferrous ions. Such reactions may also take place when e.g. $^{57}Fe(CN)_6^{3-}$ is formed in a Mössbauer source containing Fe^{2+}.

As discussed before (sects. 2.4 and 5.1) the relative resonance intensities do not necessarily represent the yields of the corresponding ^{57}Fe-species. However, for a series of related compounds it is reasonable to assume that the ratios between the intensities can be used to demonstrate a general tendency, since they are probably off by a common factor.

If the chemical effect of the $^{57}Co(EC)^{57}Fe$-reaction in $^{57}Co(CN)_6^{3-}$ was a ligand flip - i.e. the formation of an $^{57}Fe(CN)_5(NC)^{3-}$-complex, one would expect the yield of this species to increase with the affinity of the cations for the carbon end of the CN-ligand [S17, B25]; in particular, large yields should be

expected in the salts containing Fe^{2+} and Co^{2+}. Such a correlation was not observed, and it is therefore not probable that a complete 180^{o} turn of the CN-ligand takes place. On the other hand, a small twist - as proposed to explain ESR-spectra of irradiated hexacyanides (cf. sect. 5.4) - is not compatible with the large quadrupole splitting observed in the source spectra. We therefore conclude that the $^{57}Co(EC)^{57}Fe$ causes the complete decoupling of a CN-ligand to form $Fe^{III}(CN)_5^{2-}$ or $Fe^{II}(CN)_5^{3-}$.

The ratio between the resonance intensities of pentacyanides and hexacyanides in the source spectra appeared to increase with the third ionization potential [S4] of the cation in the source, i.e. with the energy required to capture electrons from the cations (fig. 18).

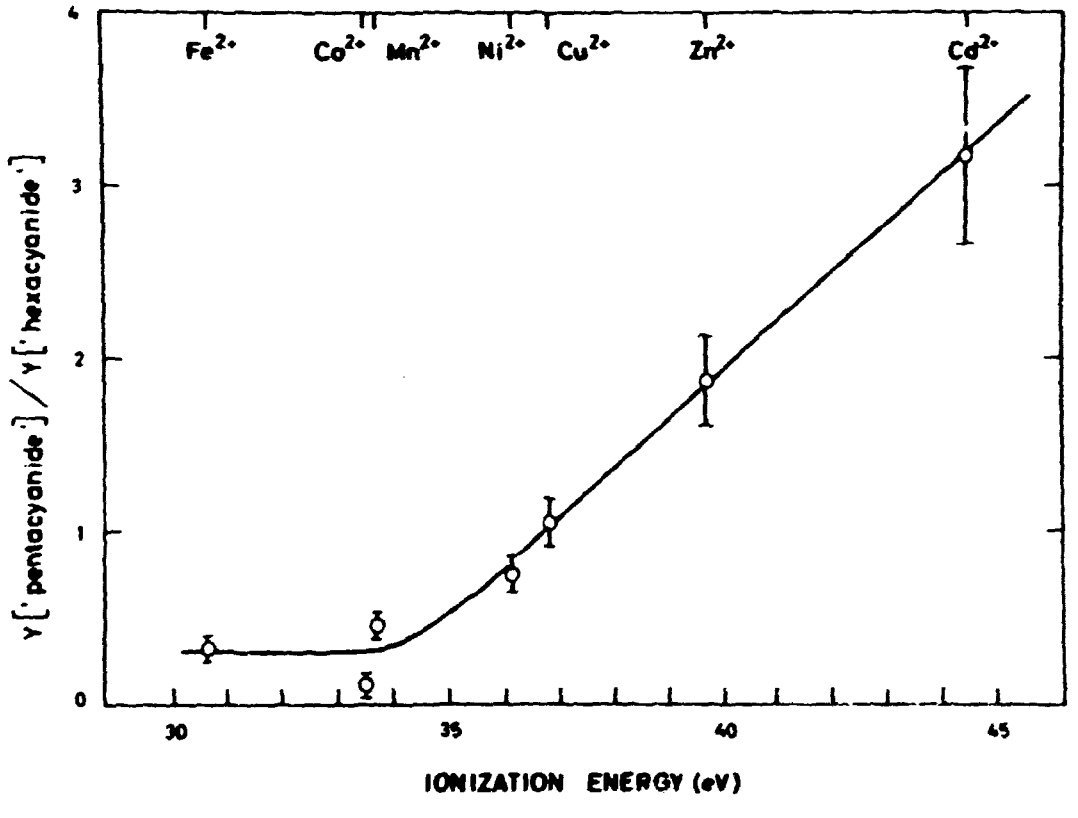


Fig. 18. The ratio between the intensities of the resonances attributed to pentacyanides and to hexacyanides plotted versus the third ionization energy of the cation in the source [F16]

We interpret this correlation by assuming that a fragmentation:

$$Fe(CN)_6^n \rightarrow Fe(CN)_5^m + CN^{n-m}$$

is caused by Coulomb repulsion following the Auger charging, but that it can be prevented if the missing electrons are supplied sufficiently rapidly from the surrounding cations. The CN-ligands readily transfer electrons [S18], and it has been shown [B22] that the activation energy for electronic conduction increases with the ionization energy of the cation in the cobaltihexacyanides in question.

As discussed above (sects. 2.4 and 5.1) the crucial point in any hot study based on Mössbauer spectroscopy is the question of the f-factors of the nascent species. Since these f-factors depend upon the temperature of the lattice, a recording of the spectra at various temperatures may yield valuable information. For such a study [F18] was chosen $Cd_3[^{57}Co(CN)_6]_2 \cdot 12H_2O$, which had (cf. fig. 18) shown a high yield of the alleged pentacyanide. Thermo-gravimetric analyses showed that the water in the crystal was lost gradually between about 40 and 120°C; since the source material was kept in a tightly closed container, measurements up to 50°C could be made. On the other hand measurements below liquid-nitrogen temperature were not reasonable since the high temperature approximation for the f-factor (cf. sect. 2.4) ceases to be valid.

The emission spectra of $Cd_3[^{57}Co(CN)_6]_2 \cdot 12H_2O$ recorded above ~150°K could be satisfactorily accounted for with the two previously observed doublets which were ascribed to $^{57}Fe(CN)_6^{3-}$ and $^{57}Fe(CN)_5^{2-}$. At lower temperatures, however, it was necessary to assume an extra resonance at -3 mm s^{-1}. Since no species with such a large isomer shift are known, we assumed that this resonance is part of a doublet, and we consequently fitted the spectra with three doublets. With the parameters found for the low temperature spectra as initial estimates it was possible to fit three doublets also to spectra recorded at about 200 K. The quadrupole splitting of this doublet can only be determined to about 3 mm s^{-1}, since the position of one of the lines is uncertain. Similarly the isomer shift can only be estimated to about -1 mm s^{-1}. These values suggest that the doublet arises from free Fe^{2+}. Most probably the Fe^{2+} sits in the main lattice and not inside the cubic cells, since absorber spectra of $Fe_3[Co(CN)_6]_2 \cdot 12H_2O$ [M8] show that Fe^{2+} in the main lattice has a quadrupole splitting of 2.8 mm s^{-1}, whereas Fe^{2+} inside the cells has only 1.8 mm s^{-1}.

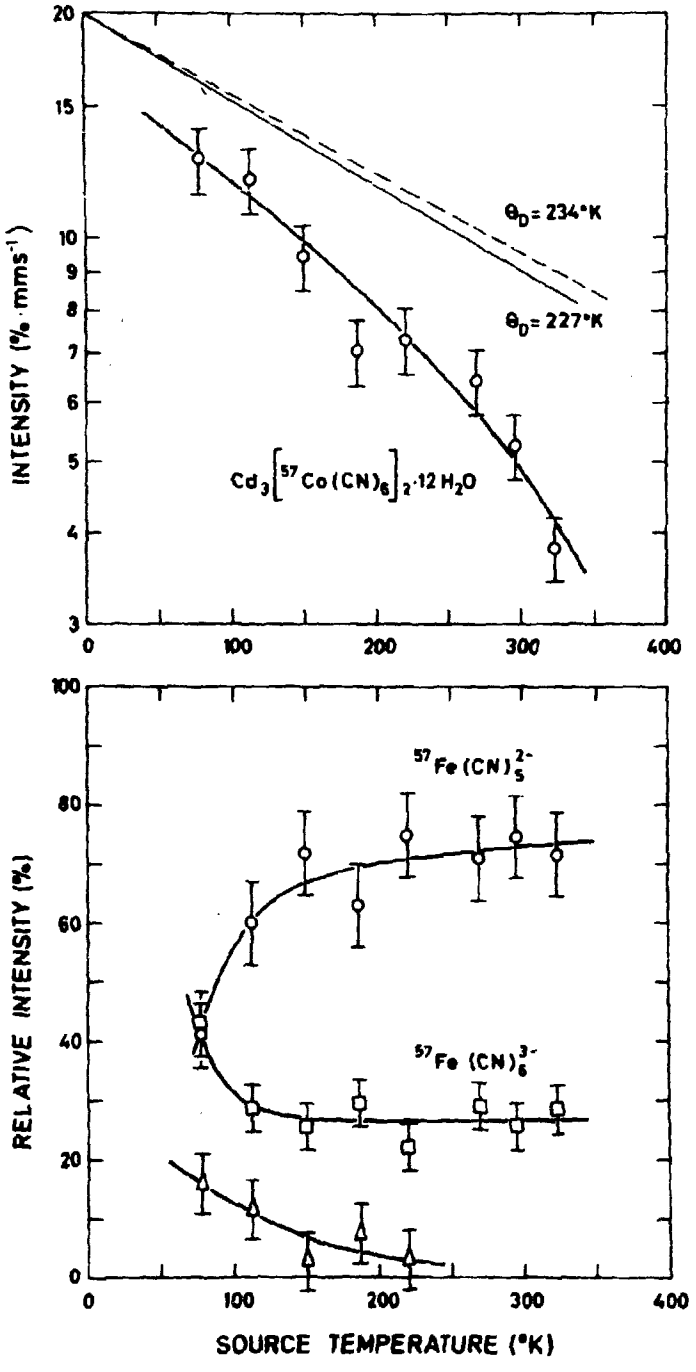


Fig. 19. Resonance intensities of the emission spectrum of $Cd_3[^{57}Co(CN)_6]_2 \cdot 12H_2O$. In the upper semilogarithmic plot the temperature dependence of the total intensity is compared with that of a $Cd_3[Fe(CN)_6]_2 \cdot 12H_2O$ absorber, shown with a dashed line. The dependence corresponding to a Debye temperature of 227 K, an average value for inorganic solids [K8], is shown in thin line. The lower plot shows the relative intensities of the three doublets in the spectra [F18].

Fig. 19 shows, in arbitrary units, the temperature dependence of the intensity of an absorber spectrum of $Cd_3[Fe(CN)_6]_2 \cdot 12H_2O$. In agreement with the expression for the f-factor (cf. sect. 2.4) the dependence is exponential. The slope of the line corresponds to a Debye temperature of 234 K; this is in good agreement with the average value for inorganic solids, 227 K, determined by Kerler [K8]. The total intensity of the source spectrum of $Cd_3[^{57}Co(CN)_6]_2 \cdot 12H_2O$ decreases much more rapidly with increasing temperature; a curve of this shape cannot be expressed as a sum of exponential functions with negative exponents, therefore we are forced to conclude that the relative yield of less tightly bonded species increases with temperature.

The lower part of fig. 19 shows how the relative intensities of the three doublets vary with the temperature of the source, and we note that the relative intensity of the alleged pentacyanide increases. This can account for the temperature dependence of the total intensity of the source spectrum if we assume that the pentacyanide is of the form $Fe^{III}(CN)_5^{2-}$, which is bonded with only five bonds in the lattice. The alternative possibility of a $Fe^{III}(CN)_5(NC)^{3-}$-species is again (cf. sect. 5.4) less likely; not only is the isocyanide bonded with six bonds, but it also appears [D2, S36] that such species are stable only at low temperatures.

On the other hand, if we assume that a CN^--ligand is lost completely by Coulomb repulsion, and that the process can be prevented by a sufficiently rapid charge transfer (cf. fig. 18), one would expect a decrease of the pentacyanide yield with temperature rather than the observed increase, the reason being that crystals of the "Prussian blue-type" are intrinsic semiconductors [D1] and that charge transfer is therefore facilitated at higher temperatures. It is, however, reasonable to assume that an expelled CN^--ligand is not displaced far from the remaining pentacyanide, since the total Coulomb energy of the charged complex may only be of the order of 25 eV. At low temperatures the fragments may recombine before emission of the Mössbauer quantum to give the present hexacyanide, whereas at higher temperatures migration of the cyanide may be facilitated and recombination prevented - consequently the yield of pentacyanide increases. However, this effect can hardly be accounted for by a continuous diffusion, since the diffusion constant is probably only of the order of 10^{-10} cm^2 s^{-1} [e.g. 04] and a formal calculation of the mean displacement in 10^{-7} s (the half life of the Mössbauer level) suggests a value of less than 1 Å [e.g. J3].

The nature of the third species, which is observed only at temperatures below 200 K, is still uncertain. The temperature dependence of the resonance intensity is consistent with a formal Debye temperature of about 100 K.

This does not agree with the behaviour observed for an Fe^{2+} ion in the main lattice, since absorber spectra of $KFe[Fe(CN)_6]\cdot H_2O$ [F12] show that ionic and complexed iron have nearly equal f-factors, even at room temperature. We therefore assume that the third species is unstable above 200 K; this is consistent with the assumption of CN-inversion, since isocyanides were found [D2] to be stable only at liquid-nitrogen temperature. Alternative interpretations of the asymmetry of the spectra, based on assumptions of paramagnetic relaxation or a Goldanskii-Karyagin effect (cf. e.g. ref. G8), are discussed in a forthcoming paper (J. Fenger and L. A. Frees, to be published).

If we extrapolate the total spectral intensity for the $Cd_3[^{57}Co(CN)_6]_2 \cdot 12H_2O$ source (fig. 19, upper plot) to T = 0, it is possible to calculate what the spectral intensity should have been, e.g. at room temperature, if all species had had the same f-factor as $Fe(CN)_6^{3-}$. On the basis of the experimentally observed total intensity and the observed relative intensities (fig. 19, lower plot) it is in principle possible to construct a set of equations which determine the Debye temperatures and the true yields of the species. The present data are not sufficiently accurate for a strict mathematical treatment, but they can be accounted for by assuming a Debye temperature of about 170 K for the $Fe(CN)_5^{2-}$. At room temperature the f-factor of $Fe(CN)_5^{2-}$ is then only about 50% of the f-factor for $Fe(CN)_6^{3-}$. This means that, although the relative resonance intensity of $Fe(CN)_5^{2-}$ is constant in this temperature range, the actual yield increases with temperature. At $-125^{\circ}C$ (~ 148 K), where the results presented in fig. 18 were obtained, the f-factor of the pentacyanide may be about 30% lower than that of the hexacyanide.

5.6. Summary of the Mössbauer Results and of the Comparisons with the Results of the Radiochemical Experiments

In our first publication on the hot-atom chemistry of ionic iron compounds [F8] we argued that if the role of the nuclear reaction was only to supply energy to the crystal lattice, the chemical effects of (EC)- and (n,γ)-reactions might be the same. This hypothesis was partly based on the observation that in $FeC_2O_4\cdot 2H_2O$ the yield of $^{57}Fe^{3+}$ after $^{57}Co(EC)^{57}Fe$-reactions (cf. sect. 5.3) was the same as the yield of $^{59}Fe^{3+}$ after $^{58}Fe(n,\gamma)^{59}Fe$-reactions (cf. sect. 4.1). However, the calibration measurements performed in connection with our beam experiment (sect. 5.2) showed much lower ^{57}Fe-resonance intensities after $^{56}Fe(n,\gamma)^{57}Fe$-reactions than after $^{57}Co(EC)^{57}Fe$-reactions. Therefore the (n,γ)-reactions must cause more damage to the lattice than the (EC)-reactions.

For the compounds $Fe_2(C_2O_4)_3 \cdot xH_2O$ and $K_3Fe(C_2O_4)_3 \cdot 3H_2O$, where iron is supposed to be complexed, further differences between the effects of (n, γ)- and EC-reactions appeared (cf. sects. 4.1 and 5.3); finally our experiments with compounds containing iron or cobalt occupying two different sites unambigously showed that the fate of the nascent iron atoms could be entirely different (cf. sect. 4.2 and 5.5):

The primary effects of $^{58}Fe(n,\gamma)^{59}Fe$-reactions are violent, and recoil-^{59}Fe nearly always leaves the lattice site; this is different from normal radiolytic effects, although of course in some cases the same products may result. Similar differences have been observed with $KClO_3$ and $KClO_4$ [B21], where γ-radiolysis has a much higher probability of breaking only one Cl-O bond than has (n, γ)-recoil.

Nearly all our Mössbauer results, on the other hand, can be interpreted on the basis of the assumption that the $^{57}Co(EC)^{57}Fe$-reaction - and the subsequent Auger cascade - does not lead to a displacement of the nascent ^{57}Fe. Two cases are dubious: in $[^{57}Co^{III}(dipy)_3](ClO_4)_3$ (cf. sect. 5.4) and in $Cd_3[^{57}Co^{III}(CN)_6]_2 \cdot 12H_2O$ (cf. sect. 5.5) weak resonances suggest the formation of $^{57}Fe^{2+}$. At least in the latter case, however, it is possible that the ^{57}Fe remains in the lattice site and that it is the ligands that are displaced.

Generally the $^{57}Co(EC)^{57}Fe$-events and application of "external" irradiation lead to formation of similar species, but whereas radiolysis reactions are normally initiated by a simple electronic excitation, this is not necessarily the case for reactions following the EC-decay. Reactions in hexacyanides were studied in most detail (cf. sects. 5.4 and 5.5) and were found to result predominantly in the formation of a pentacyanide. The mechanism is probably a "Coulomb explosion" following the Auger charging (cf. sect. 1.3); the fragments are not separated far and may even recombine before being detected, i.e. within 10^{-7} s. These speculations are supported by results reported for various other systems; they generally indicate that the amount of energy released in Auger processes is just about large enough to cause chemical effects that are detectable. Thus the isomeric transition $^{80m}Br \rightarrow {}^{80g}Br$ has been studied in a series of ions with bromine as a ligand, and the yield of free ^{80g}Br decreases with the complex stability [S10, S11]; in the densely packed K_2ReBr_6 the retention is even 100% [M30]. In the cases where molecular rupture has been observed, the recoil fragments are very susceptible to thermal annealing, both for bromine ligands [K4, L3] and central atom bromine [J2], and this suggests that the fragments have not been much separated. It also appears that although the

$^{68}Ge(EC)^{68}Ga$-reaction frees most of the ^{68}Ga from Ge-tetraphenyl, the ^{68}Ga does not form new "hot" products as does e.g. ^{70}Ga formed by the $^{70}Ge(n, p)^{70}Ga$-reaction [M18].

6. GENERAL SUMMARY

The investigations reviewed above have largely been concerned with chemical effects of nuclear reactions in central atoms of complex ions in solids. We feel that simple general models, like the ones discussed in the introduction, must be regarded with some scepticism, but it appears that the following features may be general for systems of this type:

An (n, γ)-reaction will nearly always lead to rupture of chemical bonds. This has been observed before in complicated systems (e.g. vitamin B12), but in simple systems the retention is normally above 10%. However, our experiments with soluble Prussian blue (cf. sects. 4.2 and 4.3) show that the retention can be below 1%. Retentions down to a few per cent were also observed in some salts of phosphorus oxyacids.

We believe that higher retentions observed in various systems can be attributed to an immediate recombination of the fragments and to annealing reactions during or subsequent to the neutron activation. Many studies have been concerned with the effect on the retention of various parameters of the lattice. The findings should not - as has sometimes been done - be interpreted in terms of "non-bond rupture", but in terms of different susceptibility to recombination and annealing.

The atom formed by an (n, γ)-reaction nearly always leaves its lattice site; this is evident from the observation of polymer phosphates in neutron-irradiated mono phosphates (cf. sect. 3.6) and from the experiments with the iron double complex (cf. sect. 4.3). Libby's "Ligand loss hypothesis" (cf. sect. 1.3) therefore seems untenable.

The recoil atom has a short range. Its actual magnitude varies with the systems in question (cf. sect. 4.3) and presumably even for a specific system depends drastically upon the direction and size of the recoil momentum (cf. sect. 1.3). A typical value of 10 Å is suggested - it agrees reasonably well with computer simulations (cf. sects. 1.4 and 3.2). Nevertheless the recoil atom must come to rest in a relatively undamaged region of the lattice since reactions with intact complex species is often observed (cf. e.g. sect. 3.8). Therefore the formation of a hot molten zone (cf. sect. 1.3) seems excluded.

We have found little evidence of direct hot reactions or "billard-ball replacements" (cf. sect. 1.3). Thus the formation of P-O-P bonds in neutron-irradiated phosphates can proceed as an addition - process with low - or no - activation energy (cf. sect. 3.4), and the formation of the $Fe(dipy)_3^{2+}$ complex ion in the iron double complex (cf. sect. 4.3) appears to be a solid-state exchange process. The formation of ironcyanide complexes in Prussian blue (cf. sect. 4.2) and the double complex (cf. sect. 4.3) is not fully understood; apparently a hot recoil-^{59}Fe atom ruptures an inactive iron hexacyanide complex, but its subsequent reactions with the liberated ligands may well be thermal.

On the whole our results agree with Müller's "Model of little disorder" (cf. sects. 1.3 and 4.3), although this model is too simple to account for detailed reactions in more complex systems like the phosphates (chapt. 3).

In view of the above observations it is not surprising that radioactive atoms which are shot into - or doped into - solids in some respects behave as atoms which are produced "in situ" by an (n, γ)-reaction.

The relations between "hot-atom chemistry" and "radiation chemistry" have often been discussed, but it is our belief that the chemical effects of (n, γ)-reactions cannot be fully explained in terms of the mechanisms known from radiolysis and photolysis, since these normally only result in a change in valency or the loss of a ligand (cf. sects. 3.1, 5.4, and 5.5). Further we feel that it is dangerous to assume that recoil fragments have the same structure as radiolytic species; this is frequently done in the literature, often on the basis of ESR-measurements. On the other hand, ESR-measurements can yield information on inactive species, with which the recoil atom may react (cf. sect. 3.1).

The chemical effects of $^{57}Co(EC)^{57}Fe$-reactions were compared with those of $^{58}Fe(n,\gamma)^{59}Fe$-reactions (cf. sect. 5.6) and found to be different. In contrast to the (n, γ)-recoil the EC-process and the associated Auger cascade have a very low probability of displacing the central atom; typically only ligand is decoupled. This effect is similar to that of radiolysis, but the mechanism may be different - in $^{57}Co(EC)^{57}Fe$-reactions in $^{57}Co(CN)_6^{3-}$ a CN-ligand appears to be decoupled by Coulomb repulsion (cf. sect. 5.5). Apparently the CN-fragment is not displaced far, since there is some evidence of a recombination reaction. This is in agreement with the observation (cf. sect. 1.3) that the lower energy limit for observable chemical effects in a solid is about 50 eV.

Concerning the experimental techniques the following observations were made.

In studies of (n, Y)-reactions it is of great importance that the neutron irradiations are made at low temperature and with the lowest possible dose of concurrent Y-radiation. In all the cases where we have been able to compare our results with those of other researchers, we have been led to the conclusion that their samples may have been partly annealed. As discussed in connection with P-O-P bond formation and stabilization, this may lead to erroneous conclusions (cf. sect. 3.6). In a few cases, typically with the iron oxalates (cf. sect. 4.1), a macroscopic decomposition of the samples is possible. This can be checked by control experiments with labelled compounds, but this is rarely done in hot-atom studies (cf. sect. 2.3).

The major part of our investigations of (n, Y)-reactions were made with conventional radiochemical methods (cf. sect. 2.2). A more sophisticated approach was attempted in experiments with recoil reactions in two different sites in iron compounds (cf. sects. 4.2 and 4.3). To some extent the chemical effects of the nuclear reaction were overshadowed by secondary solid-state reactions, but presumably similar experiments with more suitable compounds may yield information on primary effects, i.a. by showing to what extent annealing reactions involve the original ligands.

Mössbauer spectroscopy appears to be a convenient tool in studies of chemical effects of nuclear decay where the mechanical recoil can be ignored. It is possible to determine relative values for the f-factors of the various species formed by recording the Mössbauer spectra at different temperatures. Unfortunately, however, the interpretation of the results is complicated by the possibility that the chemical effects themselves are temperature-dependent (cf. sect. 5.5).

Mössbauer spectroscopy is not suited for studies of chemical effects of induced nuclear reactions. The number of different species that may be formed is large, and at the same time the experimental difficulties are considerable (cf. sect. 5.2); therefore reasonably accurate f-factor determinations are possible only for very simple systems (cf. sect. 5.1).

In a few cases (n, Y)-reactions lead to formation of a nucleus which subsequently decays to a Mössbauer level; this has been used by other authors (cf. sect. 2.4) to study the effects of the (n, Y)-reactions in conventional source experiments. It was assumed that if the nuclear decay - as studied with doped sources - does not have any chemical effects, then the effects observed with neutron-irradiated samples must be due to the (n, Y)-reactions. However, in the doped sources the Mössbauer atoms

occupy normal lattice positions, whereas they do not in the sources produced by neutron activation (cf. sect. 5.2). Therefore the control is not sufficient and experiments of this type do not solve the experimental problems in studies of (n, γ)-reactions.

6.1. Conclusion

In this report a series of studies of the chemical effects of nuclear transformations, mainly in solids, have been reviewed. We investigated various systems with different experimental techniques. This has made a summary of the results difficult, but in a way it reflects a general situation where the field is breaking up into various, not closely related, subjects. Of these, especially two have been treated in this report: (1) Radiochemical investigations of (n, γ)-reactions in solids, and (2) Mössbauer investigations of nuclear decay.

Chemical effects of (n, γ)-reactions in solids have been studied for many years, and it is doubtful whether further experiments can be of theoretical value. Normally the radioactive atom breaks all chemical bonds and its subsequent reactions depend mostly upon the matrix; therefore these reactions may be studied more conveniently e.g. with doped material. On the other hand, further studies can still be of interest from a practical point of view since recoil effects may play a role in connection with production, separation, and measurements of radioactive isotopes.

Studies of chemical effects of nuclear decay seem much more promising. These effects can be related to radiolysis and may thus yield valuable information on fundamental processes. Furthermore they can in many cases be studied by the attractive experimental tool: Mössbauer spectroscopy.

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Last, but not least, I want to thank K. E. Siekierska for pleasant and fruitful collaboration in the years 1967-72 when most of the above-described investigations were carried out.

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DANSK RESUMÉ

Kernereaktioner vil normalt have kemiske konsekvenser for det atom, hvori den reagerende kerne befinder sig; studiet af sådanne atomers skæbne udgør en væsentlig del af den såkaldte "hot-atom" kemi, der igen er beslægtet med strålingskemi. Hvis kernereaktionerne finder sted i et fast stof, fås et kompliceret begivenhedsmønster, der afhænger af kernereaktionen, stoffets struktur og en lang række andre faktorer. Disse effekter vil normalt kun kunne iagttages, hvis kernereaktionen fører til dannelse af en ustabil isotop - typisk vil dette være tilfældet ved neutronaktivering.

Den foreliggende rapport er en oversigt over nogle eksperimentelle undersøgelser inden for det ovenfor skitserede felt. Den er baseret på en række tidligere offentliggjorte arbejder, der - såvel i teksten som i litteraturlisten pp. 98 - 113 - er markeret ved en understregning af referencenummeret; de vigtigste er yderligere angivet med fulde titler i "Preface" pp. 7 - 8.

Hovedparten af kapitel 1 er en generel introduktion til den del af "hot-atom" kemien, der har relation til de senere refererede eksperimenter. Det vises desuden, at kemiske virkninger af kernereaktioner kan have betydning på en række områder og undertiden kan anvendes praktisk. Endelig defineres undersøgelsernes målsætning: Først og fremmest skal betydningen af det faste stofs struktur undersøges; derefter skal de kemiske virkninger af kernereaktioner sammenlignes med radiolyse i de samme og tilsvarende forbindelser.

I kapitel 2 diskuteres de eksperimentelle metoder, der kan benyttes ved sådanne undersøgelser; specielt beskrives en facilitet, hvori små prøver kan reaktorbestråles ved lav temperatur under veldefinerede betingelser. Den uundgåelige γ-stråling i en reaktor kan maskere de kemiske virkninger af neutronindfangning, bl. a. gennem makroskopisk radiolyse af prøverne. En sådan uønsket effekt kan afsløres ved kemisk analyse af radioaktivt mærkede, γ-bestrålede forbindelser; herved fås også en vis kontrol af den kemiske analysemetode.

I kapitel 3 refereres en række undersøgelser af kemiske virkninger af $^{31}P(n, \gamma)^{32}P$-reaktioner i phosphoroxyanioner. Som analysemetode blev anvendt højspændings-papirelektrophorese, hvorved det er muligt at adskille op til fjorten forskellige ^{32}P-mærkede anioner.

Forsøg med reaktorbestråling af vandige phosphatopløsninger viser, at P-O-P bindinger kan dannes ved termiske reaktioner mellem et ^{32}P-holdigt molekylefragment og en inaktiv phosphation. Forsøg med salte af phosphoroxyanioner sandsynliggør, at lignende processer kan finde sted i faste stoffer. Anioner med P-P bindinger optræder med størst udbytte i vandfri krystaller og dannes - hvis overhovedet - kun i opløsninger, når disse er meget koncentrerede. Det er derfor rimeligt at antage, at dannelse af en P-P binding kræver en kinetisk energi, der formentlig bruges til først at fjerne et iltatom fra en phosphation. Det er i denne forbindelse interessant, at ESR-målinger på reaktorbestrålet $NH_4H_2PO_4$ viser, at rekylatomer fra $^{14}N(n, p)^{14}C$-reaktioner giver anledning til dannelse af orienterede PO_3^{2-}-radikaler.

$^{31}P(n, \gamma)^{32}P$-reaktioner i phosphater har ofte været studeret; flere af de her refererede resultater viser imidlertid, at tidligere undersøgelser har været baseret på delvis annealede prøver, hvilket i nogle tilfælde har ført til fejlagtige konklusioner.

Kapitel 4 omhandler radiokemiske undersøgelser af $^{58}Fe(n, \gamma)^{59}Fe$-reaktioner. Først refereres en serie konventionelle undersøgelser af reaktioner i ferrosulfat, ferrooxalat, ferrioxalat og kalium-tris-oxalatoferrat - de er i det væsentlige foretaget med henblik på sammenligning med Mössbauer målinger refereret i kapitel 5.

I en anden type forsøg, refereret senere i kapitlet, udnyttes de muligheder, der ligger i, at jern har en række stabile og ustabile isotoper, og at flere forbindelser indeholder jern i to forskellige positioner. Man kan derfor lade den samme kernereaktion finde sted forskellige steder i et specifikt isotopberiget krystalgitter. Forsøg med specifikt ^{58}Fe-beriget $KFe[Fe(CN)_6]\cdot H_2O$ og $[Fe(dipy)_3]_3[Fe(CN)_6]_2\cdot 1\text{-}3H_2O$ viser, at det dannede ^{59}Fe i de fleste tilfælde bryder alle kemiske bindinger; ved annealing sker der endvidere i visse tilfælde ikke nogen rekombination med de oprindelige ligander. Rekylatomets oprindelige kemiske form er således uden større betydning. På den anden side vil gitterets struktur og komponenter selvfølgelig afgøre, i hvilke nye kemiske forbindelser ^{59}Fe kan indgå.

Radiokemiske analyser har den alvorlige svaghed, at de kræver destruktion af den prøve, hvori kernereaktionerne har fundet sted; der har derfor været en voksende interesse for anvendelse af forskellige fysiske målemetoder. Den mest lovende er Mössbauer spektroskopi, og en række forsøg med anvendelse af denne teknik refereres i kapitel 5.

Først beskrives et reaktor forsøg, hvor et target af $Fe(COO)_2 \cdot 2H_2O$ eller $K_4Fe(CN)_6 \cdot 3H_2O$ blev bestrålet med termiske neutroner og samtidig anvendt som kilde i et Mössbauer forsøg. Herved skulle det i princippet være muligt at studere kemiske virkninger af $^{56}Fe(n,\gamma)^{57}Fe$-reaktioner; imidlertid viste det sig, at Mössbauer resonanserne var svagere end beregnet. Herved underbygges konklusionen fra de radiokemiske forsøg, som viste, at rekylatomer forlader deres position i krystalgitteret, men det må samtidig erkendes, at netop denne effekt kan gøre en mere detaljeret undersøgelse umulig.

Mössbauer spektroskopi viste sig at være langt bedre egnet til undersøgelse af $^{57}Co(EC)^{57}Fe$-henfald, hvor de kemiske virkninger formodes at skyldes udløsning af en Auger kaskade. Flere forsøg bl. a. med specifikt doped $KFe[Fe(CN)_6] \cdot H_2O$ viser, at det dannede ^{57}Fe ikke forlader sin gitterposition, og at ændringerne i omgivelserne er små. Mest detaljeret studeredes EC-henfald i $^{57}Co(CN)_6^{3-}$, der medfører dannelse af $^{57}Fe(CN)_5^{2-}$ - d. v. s. afkobling af en ligand. Ved at variere komponenterne i den omgivende krystal vises det, at sandsynligheden for denne proces afhænger af, hvor hurtigt de tabte elektroner kan genindfanges; dette støtter en antagelse om, at ligandtabet skyldes Coulomb frastødning.

I kapitel 5 summeres resultaterne. Det konkluderes, at (n, γ)-reaktioner i centralatomer kan få disse til at bryde alle bindinger til de omgivende ligander. I et fast stof vil rekylatomet forlade sin gitterposition og indgå i kemiske reaktioner, der stort set er uafhængige af det rekylerende atoms oprindelige kemiske form og næsten udelukkende bestemmes af det omgivende gitter. Disse effekter er væsensforskellige fra radiolyse, der i faste stoffer oftest består i, at en ligand afkobles, medens centralatomet bliver siddende i en næsten uændret gitterposition.

De kemiske virkninger af kernereaktioner, der medfører udløsning af en Auger-kaskade, minder derimod mere om radiolytiske effekter, selv om de underliggende mekanismer kan være forskellige.